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HYDROGEN ION IMPLANTATION INDUCED LOW RESISTIVE $KNbO_3$ LAYER IN BULK SINGLE CRYSTAL

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Abstract: Origins of low resistivity in H-ion implanted $KNbO_3$ bulk single crystals are studied by elastic recoil detection analysis (ERDA) and Van der Pauw methods. The H-ion implantation (peak ion fluence: 5.0×10^{15} cm^{-2}) into $KNbO_3$ is performed using a 500 keV implanter. The sheet resistance decreases from ~10^8 Ω/□ for an un-implanted $KNbO_3$ sample to 2.3×10^5 Ω/□ for as-implanted and 4.3×10^5 Ω/□ for 150 ºC annealed samples, respectively. The ERDA experiment using the 1.5 MeV-$^4He^+$ beam can evaluate hydrogen from the surface to around 60 nm. The hydrogen concentration near the surface estimated is 5.1×10^{14} cm^{-2} for un-implanted $KNbO_3$ sample, 5.6×10^{14} cm^{-2} for as-implanted, 3.4×10^{14} cm^{-2} for 150 ºC annealed samples, respectively, indicating that a part of hydrogen is diffused out by annealing. The low resistive layer induced in H-ion implanted $KNbO_3$ suggests the existence of a shallow energy level related to the complex defect consisting of hydrogen interstitial and the proton induced defect such as oxygen vacancy.

I. Introduction

In the development of ferroelectric material, lead is the most important element. The lead-based ferroelectric material such as lead zirconate titanate (PZT) is used in large numbers. It has excellent properties, however, because it contains harmful lead, influence on the environment is concerned. Recently, in order to address this problem, high-performance lead-free material that can be used as a substitute material for PZT is expected. $KNbO_3$ is one of the lead-free ferroelectric materials.

In the meantime, the ferroelectric field-effect transistor uses the surface conduction of insulating ferroelectric under the gate oxide [1, 2)]. Our recent study of ZnO reported the decrease in resistivity from 2.5×10^3 Ωcm for un-implanted ZnO to 6.5 Ωcm for H-ion implanted one [3)]. In the present study, we artificially form a surface conducting layer in $KNbO_3$ by the H-ion implantation and report the decrease in resistance in H-ion

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implanted $KNbO_3$ using elastic recoil detection analysis (ERDA) and Van der Pauw technique [4].

II. Experimental

The (001) oriented $KNbO_3$ bulk single crystals were used in the present study. $KNbO_3$ is a unique dielectric material with four phase transitions, namely rhombohedral (T< -10 ^oC), orthorhombic (-10 ^oC < T < 225 ^oC), tetragonal (225 ^oC < T < 435 ^oC), and cubic (T > 435 ^oC) [5]. $KNbO_3$ shows ferroelectricity below 435 ^oC. Figure 1 shows the perovskite $KNbO_3$ (orthorhombic) structure in the vicinity of room temperature. In particular, this material cannot maintain single-crystallinity by the rapid heating and cooling. The lattice constant at room temperature is a = 5.695, b = 5.721, and c = 3.974 Å [6]. Ion energies and the corresponding ion fluence were selected to obtain a uniform depth profile according to the TRIM (Transport of Ions in Matter) simulation of the projected range on the ions (see Fig. 2) [7]. The H-ion implantation into $KNbO_3$ was performed using an energy of 500 keV (ion fluence: 5.0×10^{15} cm^{-2}). The resulting implantation depth and the H concentration were 3650 nm and 1.62×10^{20} cm^{-3}, respectively. The band gap of $KNbO_3$ was determined by optical absorption measurements. Following implantation, some as-implanted $KNbO_3$ samples were annealed at temperatures ranging from 100 to 150 ^oC for 1 hour in nitrogen atmosphere to prevent the degeneration of crystallinity due to phase transition. In sheet resistance measurements using Van der Pauw technique [4], electrodes are fabricated using titanium/gold. Hydrogen in H-ion implanted $KNbO_3$ was evaluated by ERDA using a 1.5 MeV $^4He^+$ beam. The recoiled H-ions were detected with a solid-state detector located at 15^o. An aluminum foil with 7.5 μm in thickness was placed in front of the ERDA detector in order to stop all the recoiled atoms heavier than hydrogen.

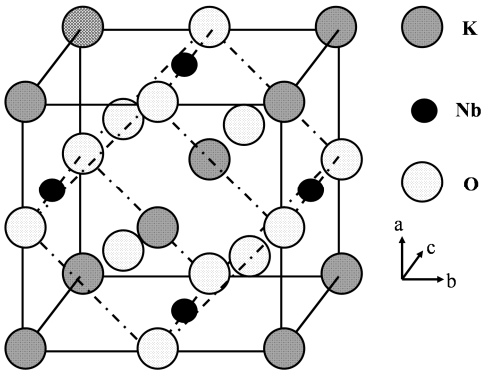

Fig 1. Crystal structure of perovskite (orthorhombic) $KNbO_3$ at room temperature.

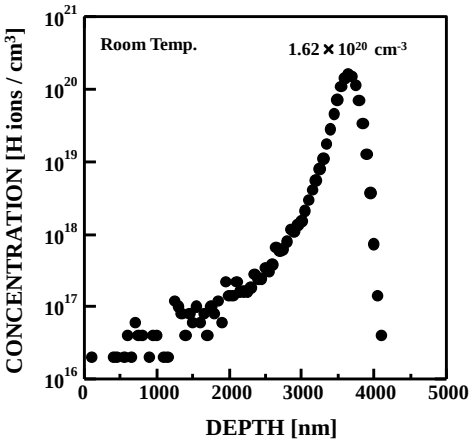

Fig 2. Simulated depth profile with the TRIM code of H ions implanted into $KNbO_3$ for acceleration energy and fluence; energy: 500 keV, fluence: 5.0×10^{15} cm^{-2}.

III. Results and discussion

The change in the optical absorbance was not observed before and after H-ion implantation. Therefore, the band gap of $KNbO_3$ did not change by the H-ion implantation. The band gap of $KNbO_3$ estimated by an optical absorption measurement is 3.16 eV (392 nm) at room temperature (see Fig. 3 (a, b)).

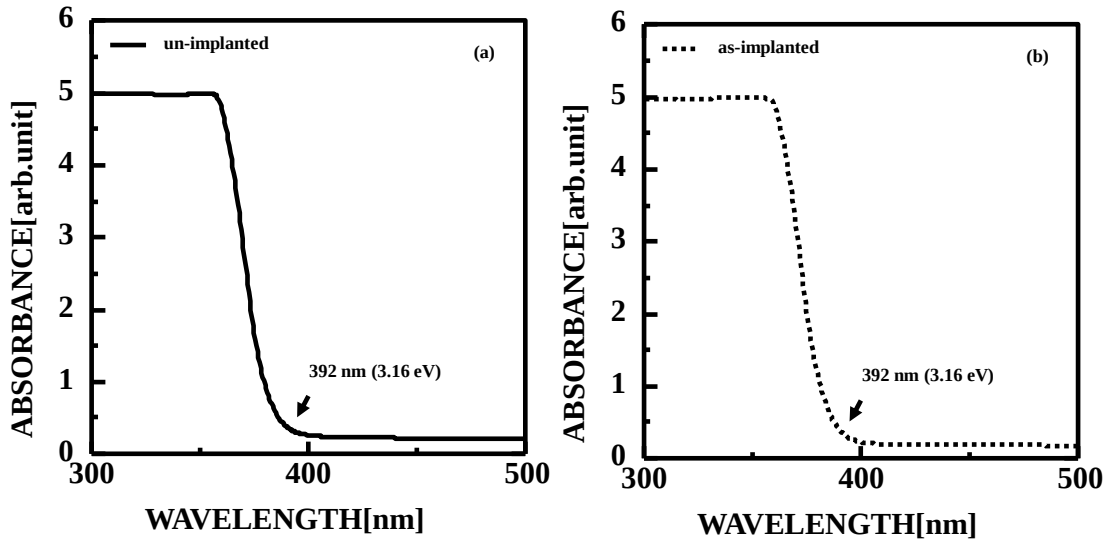

Fig 3. Optical absorption spectra of $KNbO_3$, (a) un-implanted, (b) as-implanted

Table 1 shows the sheet resistance of the un-implanted and as-implanted samples. The sheet resistance of un-implanted samples was high ($>10^8$ Ω/□). After the H-ion implantation, the sheet resistance decreased by three orders of magnitude to 2.3×10^5 Ω/□. The decrease would be attributed to a shallow energy level related to the complex defects consisting of hydrogen interstitials and vacancy defect such as the oxygen vacancy (V_O) generated by the H-ion implantation as described later. After subsequent annealing at 100 ºC and 150 ºC, the sheet resistances were 2.3×10^5 Ω/□ and 4.3×10^5 Ω/□, respectively. The higher sheet resistance of 150 ^oC annealed samples indicates that a part of hydrogen was diffused out by annealing as described later.

Table 1. The sheet resistance of un-implanted, H-ion implanted $KNbO_3$, 100 ^oC and 150 ^oC annealed $KNbO_3$.

	Sheet resistance [Ω/□]
un-implanted	**$> 10^8$**
as-implanted	**2.3×10^5**
100 ºC-annealed	**2.3×10^5**
150 ºC-annealed	**4.3×10^5**

The hydrogen behavior was calculated by the following process [8]. The transition energy E_1 of hydrogen recoiled at the surface is

$$E_1 = E_0 [4(M_1M_2) / (M_1 + M_2)^2] \times (\cos \theta)^2, \quad (1)$$

where E_0 is the energy of the incident helium ion (1.5 MeV), M_1 and M_2 the mass of hydrogen and helium, and θ the recoil angle. The energy E_2 of helium recoiled at the depth (t) is

$$E_2 = 1.5 - (dE_{He} / dx) \times (t / \sin (\theta/2)), \quad (2)$$

where (dE_{He} / dx) is energy loss of helium ion in $KNbO_3$. The energy E_3 of hydrogen at the depth (t) is

$$E_3 = E_2 [4(M_1M_2) / (M_1 + M_2)^2] \times (\cos \theta)^2, . \quad (3)$$

The energy E_4 of the recoiling hydrogen at the detector is

$$E_4 = E_3 - (dE_H / dx) \times (t / \sin (\theta/2)), \quad (4)$$

where (dE_H / dx) is energy loss of hydrogen ion in $KNbO_3$. With ERDA experiment using 1.5 MeV-Van de Graaff accelerator of Hosei University, the hydrogen concentration can be evaluated from the surface to around 60 nm in depth. Therefore, H concentration was calculated at 60 nm in depth. Figure 4 shows the hydrogen distribution estimated from ERDA measurements for the un-implanted, as-implanted and 150 ºC annealed samples. In un-implanted samples, hydrogen was observed, suggesting that hydrogen was introduced during the crystal growth of $KNbO_3$. In 150 ºC annealed samples, the hydrogen yields were lower than as-implanted samples, suggesting that a part of hydrogen was diffused out by annealing.

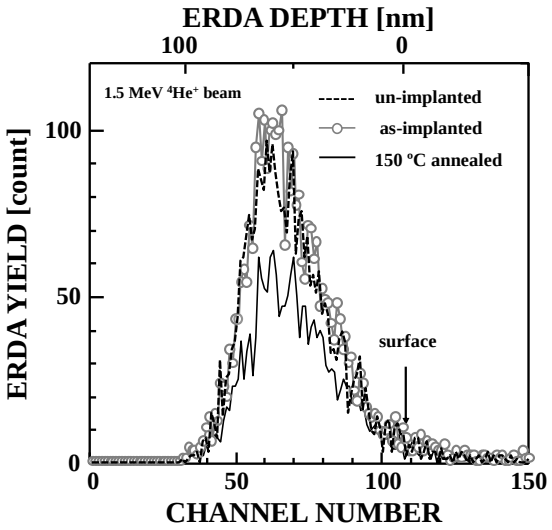

Fig 4. ERDA spectra using 1.5 MeV $^4He^+$ ions for un-implanted, H-ion implanted, and 150 ºC annealed samples.

The hydrogen concentration at 60 nm from the surface was calculated by the following equation.

$$Y = [NQ (d\sigma / d\Omega) \Delta\Omega] / \sin \theta/2, \quad (5)$$

where Y is the yield of recoiled hydrogen near the surface, N the hydrogen concentration, Q the number of incident $^4He^+$ ions (9.4×10^{12} for the present study), $(d\sigma / d\Omega)$ [9] the differential scattering cross section, ΔΩ solid angle of detector (9.8 mrad), and θ the recoil angle (30^o). Table 2 shows the hydrogen concentrations of $KNbO_3$ at 60 nm of the un-implanted and as-implanted samples. In these samples,

hydrogen concentrations were 5.1 × 10^{14} cm^{-2} and 5.6 × 10^{14} cm^{-2}, respectively. After the subsequent annealing at 150 ºC, the hydrogen concentration reduced to 3.4 × 10^{14} cm^{-2}, suggesting that a part of hydrogen was diffused out by annealing.

Table 2. The hydrogen concentrations of $KNbO_3$ estimated at 60 nm in depth.

	Hydrogen concentration[cm^{-2}]
un-implanted	**5.1 × 10^{14}**
as-implanted	**5.6 × 10^{14}**
150 ºC-annealed	**3.4 × 10^{14}**

The present ERDA study shows the out diffusion effects due to the thermal annealing on hydrogen included in a thin surface layer. The hydrogen concentration is same orders of 10^{14} cm^{-2} for un-implanted and as-implanted samples, while the resistance after H-ion implantation and annealing is three orders of magnitude lower than that of un-implanted samples. Therefore, the low resistive layer in H-ion implanted samples suggests the existence of a shallow energy level related to the complex defect consisting of hydrogen interstitial and the proton induced defect such as V_O. The V_O defect has been reported in the hydrogen implanted ZnO bulk single crystal [10].

IV. Conclusion

The H-ion implantation into $KNbO_3$ bulk single crystals was performed using an energy of 500 keV (ion doses: 5.0 × 10^{15} cm^{-2}). The band gap of $KNbO_3$ bulk single crystals did not change by the H-ion implantation. The band gap of $KNbO_3$ estimated by optical absorption measurements was 3.16 eV (392 nm). The sheet resistance of H-ion implanted $KNbO_3$ bulk single crystals changed from >10^8 Ω/□ for un-implanted samples to 2.3 × 10^5 Ω/□ for as-implanted ones. The low resistive layer induced in H-ion implanted $KNbO_3$ suggests the existence of a shallow energy level related to the complex defect consisting of hydrogen interstitial and the proton induced defect such as oxygen vacancy. The sheet resistance of 150 ºC annealed samples decreased to 4.3 × 10^5 Ω/□ from the as-implanted samples of 2.3 × 10^5 Ω/□. From ERDA measurements, the slight increase in sheet resistance in the 150 ºC annealed samples was related to the out diffusion of hydrogen. The present study suggests the potential application of the H-ion implanted $KNbO_3$ layer with low resistivity as a surface conduction layer of insulating ferroelectric under the gate oxide.

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