

Persistent photoconductivity in hydrogen ion-implanted KNbO₃ bulk single crystal

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Abstract. Persistent Photoconductivity (PPC) in hydrogen-ion implanted (001) oriented KNbO₃ bulk single crystals (perovskite structure at room temperature; ferroelectric with a band gap of 3.16 eV) is studied in air at room temperature to prevent the crystallinity degradation caused by the phase transition. Hydrogen is implanted into KNbO₃ bulk single crystals using the energy (the peak ion fluence) of 500 keV ($5.0 \times 10^{15} \text{ cm}^{-2}$). The resistivity varies from $\sim 10^8 \Omega/\square$ for an un-implanted KNbO₃ sample to $2.3 \times 10^5 \Omega/\square$ for as-implanted one, suggesting the presence of donors consisting of hydrogen interstitial and oxygen vacancy. The PPC is clearly observed with ultraviolet and blue LEDs illumination rather than green and infrared, suggesting the release of electrons from the metastable conductive state below the conduction band relating to the charge states of the oxygen vacancy as observed in electron irradiated ZnO.

1. Introduction

The ferroelectric field-effect transistor uses the surface conduction of insulating ferroelectric under the gate oxide. In the previous study, we artificially formed a surface conducting layer in KNbO₃ (perovskite structure, $a=5.697$, $b=3.971$, and $c=5.722 \text{ \AA}$ at room temperature) by the hydrogen ion-implantation [1]. Persistent Photoconductivity (PPC) in electron irradiated ZnO bulk single crystal has been studied using light emitting diodes (LEDs) with various wavelengths above and below the band gap [2]. Irradiation induced oxygen vacancy (V_{O}) plays an important role in PPC. However, there are few reports on the PPC phenomena in ferroelectric material. The PPC has been observed in the layered perovskite Nd₂Ti₃O₉ [3] and the Niobate nanosheets [4] under the vacuum condition, suggesting the presence of the surface oxygen vacancy evidenced by the disappearance of PPC phenomenon in the ambient air. Lead zirconate titanate (PZT) has excellent properties, however, it contains harmful lead and, thus influence on the environment is concerned. KNbO₃ is expected as a substitute material for PZT. KNbO₃ is a unique dielectric material that has four phase transitions, namely rhombohedral ($T < -10 \text{ }^\circ\text{C}$), orthorhombic ($-10 \text{ }^\circ\text{C} < T < 225 \text{ }^\circ\text{C}$), tetragonal ($225 \text{ }^\circ\text{C} < T < 435 \text{ }^\circ\text{C}$), and cubic ($T > 435 \text{ }^\circ\text{C}$) [5]. KNbO₃ shows ferroelectricity below 435 °C. However, this material cannot maintain single-crystallinity by the rapid heating and cooling. In the present study, we report the PPC observed in hydrogen-ion implanted KNbO₃ bulk single crystals at room temperature in air.



2. Experiments

The (001) oriented KNbO_3 bulk single crystals were purchased from SurfaceNet GmbH, Germany. The energy band gap of KNbO_3 estimated from optical absorption is 3.16 eV [1]. The hydrogen concentration near the surface of KNbO_3 evaluated by elastic recoil detection analysis (ERDA) using a 1.5 MeV $^4\text{He}^+$ beam was $5.1 \times 10^{14} \text{ cm}^{-2}$ for un-implanted sample [1]. Therefore, the residual hydrogen was recognized in un-implanted samples.

Hydrogen-ion implantation was performed using an energy of 500 keV (ion fluence: $5.0 \times 10^{15} \text{ cm}^{-2}$). During implantation the samples were kept at room temperature. The resulting implantation depth and the hydrogen concentration were 3650 nm and $1.62 \times 10^{20} \text{ cm}^{-3}$, respectively. The hydrogen concentration at around 60 nm from the surface evaluated by ERDA was $5.6 \times 10^{14} \text{ cm}^{-2}$ for as-implanted and 100 °C annealed samples [1]. In sheet resistance measurements using Van der Pauw technique, electrodes were fabricated using titanium/gold. The resistance varied from $>10^8 \Omega/\square$ for an un-implanted sample to $2.3 \times 10^5 \Omega/\square$ for as-implanted and 100 °C annealed ones. The decrease in resistance would be attributed to a donor related to the complex defects consisting of hydrogen interstitials and vacancy defect such as V_{O} generated by the hydrogen-ion implantation. This situation has been observed in the H-ion implanted ZnO [6].

For the PPC measurements, samples were kept at room temperature in air to maintain single-crystallinity by the rapid heating and cooling, and then illuminated with an ultraviolet-emitting diode (a peak wavelength of $\lambda=400 \text{ nm}$) for the excitation above the energy band gap. The measurements for excitation below the band gap were also performed in comparison with the illumination above the energy gap, using blue ($\lambda=465 \text{ nm}$), green (520 nm), and infrared (940 nm) emitting diodes.

3. Result & Discussion

Figure 1 shows the PPC of 100 °C annealed samples taken at room temperature in air for the illumination with various LEDs. Although twice on- and off-operations using the blue and green LEDs were tried, similar decay curve was observed. The photocurrent for the excitation above the energy band gap using a ultraviolet LED increases more in comparison with those below the band gap, showing the effective excitation from the valence band and/or the neutral oxygen vacancy (V_{O}^0) level to the conduction band. Furthermore, for the excitation below the band gap the photocurrent using the blue LED is larger than those using other LEDs. This suggests the presence of photo-responsive

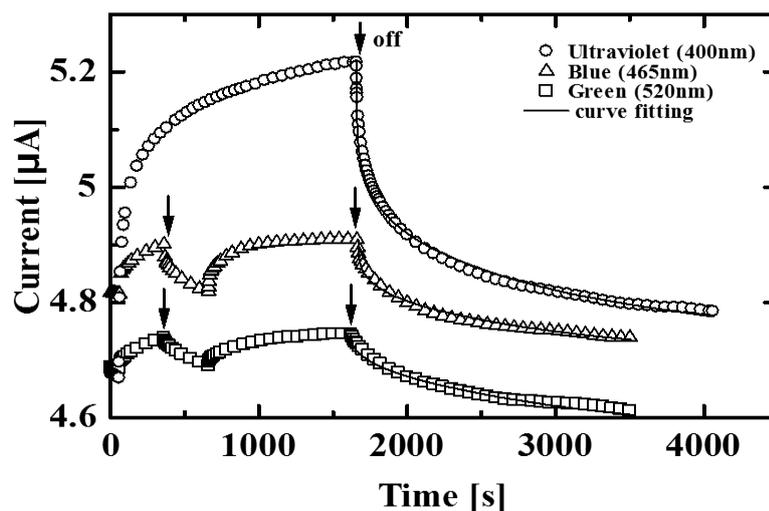


Figure 1. Persistent photoconductivity taken at room temperature in air for the illumination with various LEDs. The solid curves show the curve fitting with Eq.(1).

defects such as V_O for blue band region located at around 2.6 eV from the valence band. The decay kinetics of PPC seen here follow stretched exponential functions as described in previous works [7],

$$I_{PPC}(t) = I_{PPC}(0) \exp[-(t/\tau)^\beta], \quad (\beta < 1), \quad (1)$$

where $I_{PPC}(0)$ is the factor defined as the PPC build up level at the moment of light excitation being removed, τ is the PPC decay time constant, and β is the decay exponent. The solid curves in Fig.1 are the least squares fit of data with Eq.(1). Table 1 shows τ and β values for some LED illuminations. Table 2 also shows the percentage value of the PPC measured at 600 sec after cut off of the LED light. This indicates that the illumination due to LEDs above and near the band gap induces the effective PPC phenomenon.

Table 1. Decay time constant (τ) and decay exponent (β) for each LED estimated by eq.1

LED (wavelength; nm)	Decay time constant (τ ; sec)	decay exponent (β)
Ultraviolet (365)	1.0×10^6	0.28
Blue (470)	1.2×10^8	0.247
Green (520)	4.8×10^7	0.279
Infrared (950)	1.7×10^5	0.48

Table 2. Percentage value of the PPC measured at 600 sec after cut off of the LED light.

LED (wavelength; nm)	Percentage value of the PPC (%)
Ultraviolet (365)	63.7
Blue (470)	56.3
Green (520)	41.4
Infrared (950)	14.4

The perovskite KNbO_3 ($\text{K}^1\text{Nb}^5\text{O}^2_3$) structure has the K cation in 12-fold coordination surrounded by O anions, and the Nb cation in 6-fold coordination surrounded by an octahedron of O anions. PPC phenomenon in KNbO_3 would be expected to occur in the similar origin as PPC in ZnO [2]. According to the Lany and Zunger's model [8] for PPC in ZnO ($\text{Zn}^{2+}\text{O}^{2-}$) (see Fig.2), the V_O^0 creates a defect localized state (DLS) deep in the band gap, which localizes two electrons. When the two electrons at the DLS of V_O^0 are optically excited to V_O^{2+} , the Zn neighbors relax outwards and reach a configuration with a Zn-Zn distance of 4.0 Å. As a result, the DLS is shifted into the inside of the conduction band and the DLS of V_O^{2+} becomes unoccupied. Additionally, the DLS spreads and resonates with the conduction band above the conduction band minimum (CBM). The resonance of the DLS with the conduction band results in the perturbed-host state (PHS) as a metastable conductive state (MCS) near the CBM (see Fig.2 (b)). Consequently, the PHS behaves as a shallow donor state [8]. Thus, the electrons in the PHS can be easily excited to the conduction band, leading to PPC. In KNbO_3 , when the two electrons at the DLS of V_O^0 are optically excited to V_O^{2+} , the K and/or Nb neighbors would relax outwards and the DLS is shifted into the inside of the conduction band and the DLS of V_O^{2+} becomes unoccupied. This lattice relaxation is similar to the situation that lattice distortions

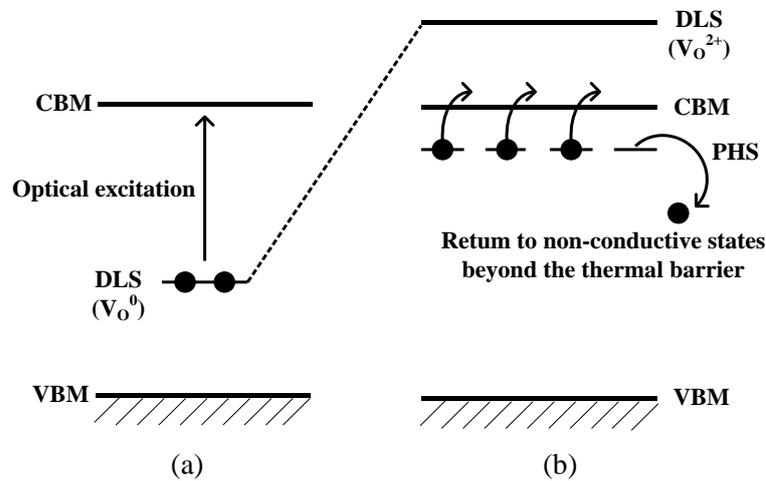


Figure 2. Schematic diagram based on Lany and Zunger's model [8]. When the two electrons at the defect localized state (DLS) of V_O^0 in the band gap are optically excited to V_O^{2+} (Fig.2 (a)), the resonance of the DLS with the conduction band results in the perturbed-host state (PHS) near the conduction band minimum (CBM) (Fig.2 (b)). The electrons in the PHS as a shallow donor state can be easily excited to the conduction band, leading to PPC.

increase in magnitude in going from the neutral to the (2+) charge state of V_O in perovskite $SrTiO_3$ [9]. As a result, electrons occupy the MCS near the CBM. In $KNbO_3$, at higher temperature such as room temperature, the thermal excitation to the CBM for the electrons in the PHS would be enhanced than that at lower temperature, causing a rapid decrease of PPC.

4. Conclusion

The Persistent Photoconductivity in hydrogen-ion implanted $KNbO_3$ bulk single crystals was observed in air at room temperature. Hydrogen was implanted into $KNbO_3$ bulk single crystals using the energy (the peak ion fluence) of 500 keV ($5.0 \times 10^{15} \text{ cm}^{-2}$). The resistivity varied from $>10^8 \Omega/\square$ for an unimplanted sample to $2.3 \times 10^5 \Omega/\square$ for as-implanted one, suggesting the presence of donors consisting of hydrogen interstitial and oxygen vacancy. The PPC was clearly observed with ultraviolet and blue LEDs illuminations rather than green and infrared ones. According to the Lany and Zunger's model for PPC in ZnO , the thermal excitation to the conduction band minimum for the electrons in the perturbed-host state near the conduction band minimum was enhanced at room temperature, causing a rapid decrease of PPC.

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