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Hydrogen interstitial in H-ion implanted ZnO bulk single crystals: Evaluation by elastic recoil detection analysis and electron paramagnetic resonance

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ABSTRACT

The origins of low resistivity in H ion-implanted ZnO bulk single crystals are evaluated by elastic recoil detection analysis (ERDA), electron paramagnetic resonance (EPR), and Van der Pauw methods. The H-ion implantation (peak concentration: 5.0×10^{15} cm^{-2}) into ZnO is performed using a 500 keV implanter. The maximum of the concentration of the implanted H estimated by a TRIM simulation is at 3600 nm in depth. The resistivity decreases from $\sim 10^3\ \Omega$ cm for un implanted ZnO to 6.5 Ω cm for as-implanted, $2.3 \times 10^{-1}\ \Omega$ cm for 200 °C annealed, and $3.2 \times 10^{-1}\ \Omega$ cm for 400 °C annealed samples. The ERDA measurements can evaluate the concentration of hydrogens which move to the vicinity of the surface (surface to 300 nm or 100 nm) because of the diffusion by the annealing at 200 °C and 400 °C. The hydrogen concentration near the surface estimated using the 2.0 MeV helium beam is $\sim 3.8 \times 10^{13}$ cm^{-2} for annealed samples. From EPR measurements, the oxygen vacancy of +charge state (V_o^+) is observed in as-implanted samples. The V_o^+ related signal ($g = 1.96$) observed under no illumination disappears after successive illumination with a red LED and appears again with a blue light illumination. The activation energy of as-implanted, 200 °C annealed, and 400 °C annealed samples estimated from the temperature dependence of carrier concentration lies between 29 meV and 23 meV, suggesting the existence of H interstitial as a shallow donor level.

1. Introduction

ZnO, with a 3.37 eV direct band gap and a large exciton binding energy of 60 meV, has been widely used for many applications such as piezoelectric transducers, varistors, and gas and ultraviolet light sensors. Recently, large single ZnO crystals grown via the hydrothermal method [1] have offered many complementary and competitive advantages to GaN, which has a bandgap and a lattice constant similar to those of ZnO. In addition, doped ZnO [2] is also expected as a transparent conductive oxide (TCO) front contact and a window layer in thin film solar cells, such as indium tin oxide and amorphous silicon photovoltaic modules. ZnO thin films have many important advantages as TCOs.

Our recent studies have reported the decrease in resistivity from $2.5 \times 10^3\ \Omega$ cm for un-implanted ZnO to 6.5 Ω cm for H-implanted ones [3]. The origin of low resistivity was attributed to the H interstitial (H_i). RBS/channeling measurements also showed that Zn interstitial is not an origin of the low resistivity. Nuclear reaction analysis measurements for as-implanted ZnO suggested the existence of the oxygen interstitial. From photoluminescence measurements, the broad green band emission was observed in as-implanted samples. This emission was mainly related to oxygen interstitial and oxygen vacancy defects.

In the present study, we investigate the behavior of hydrogen and oxygen related defects by elastic recoil detection analysis (ERDA), electron paramagnetic resonance (EPR), and Van der Pauw techniques.

2. Experimental

ZnO single crystals grown by the hydrothermal method (Tokyo Denpa co., Ltd.) were used in the present study. H-ion implantation was performed using a 500 keV implanter. During implantation, the samples were kept at room temperature. H-ions implantation into ZnO was performed using an energy of 500 keV (peak

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concentration: 5.0×10^{15} cm^{-2}) [3]. A TRIM simulation [3] showed that the maximum of the concentration of the implanted H was at 3600 nm in depth. Following implantation, some as-implanted ZnO samples were annealed at a temperature ranging from 200 °C to 400 °C for 1 h in Nitrogen atmosphere. In Hall-effect measurements using Van der Pauw technique, electrodes were fabricated using indium. Hydrogen near the surface in H-implanted ZnO was evaluated by ERDA using a 2.0 MeV ^{4}He$^+$ beam (1.5 MeV beam). The recoiled H-ions were detected with a solid-state detector located at 15°. A Myler film (7.5 μm) was placed in front of the ERDA detector in order to stop all the recoiled atoms heavier than hydrogen. The evaluation depth of the ERDA measurements in the present study was 300 nm (100 nm) from the surface for the 2.0 MeV ^{4}He$^+$ beam (1.5 MeV beam). The oxygen vacancy in H-implanted ZnO was evaluated by EPR at 77 K.

3. Results and discussion

Table 1 shows the resistivity, mobility, and carrier concentration of the implanted and unimplanted samples. H-ion implanted and annealed ZnO samples showed n-type conduction. In the unimplanted samples, the resistivity, mobility, and carrier concentration were $2.5 \times 10^3\ \Omega$ cm, 82 cm^2/Vs, and 2.9×10^{13} cm^{-3}, respectively. As shown in Table 1, the resistivity decreased by three orders of magnitude to 6.5 Ω cm following the H-ion implantation. The origin of the low resistivity in the as-implanted samples was attributed to the H_i as a shallow donor in ZnO [3]. After subsequent annealing at 200 °C and 400 °C, the resistivity decreased to 0.23 Ω cm and 0.32 Ω cm, respectively. The resistivity of 200 °C and 400 °C annealed samples were one order of magnitude lower than as-implanted samples, suggesting that the H_i was increased by annealing as described later. Therefore, the origins of the low resistivity would be attributed to H_i.

Fig. 1 shows the temperature dependence of carrier concentration at 90–360 K for as-implanted, 200 °C annealed and 400 °C annealed samples. The activation energies of these samples estimated from the slope due to the linear approximation were 29 meV, 28 meV and 23 meV, respectively. These activation energies would be related to H_i, because the estimated energies are close to the Seager's reported value, 36 ± 4 meV[4].

The hydrogen behavior was calculated by the following process [5]. 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 (2.0 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

$$E_2 = 2.0 - (dE_{He}/dx) \times (t/\sin\theta), \quad (2)$$

where (dE_{He}/dx) is energy loss of helium ion in ZnO. 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

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

Table 1
Electrical properties of un-implanted, H-ion implanted ZnO, 200 °C and 400 °C annealed ZnO.

	Resistivity (Ω cm)	Mobility (cm^2/Vs)	Carrier concentration (cm^{-3})
Un-implanted	2.5×10^3	82	2.9×10^{13}
As-implanted	6.5	7.7	1.4×10^{17}
200 °C-annealed	0.23	15.7	1.7×10^{18}
400 °C-annealed	0.32	21.3	9.0×10^{17}

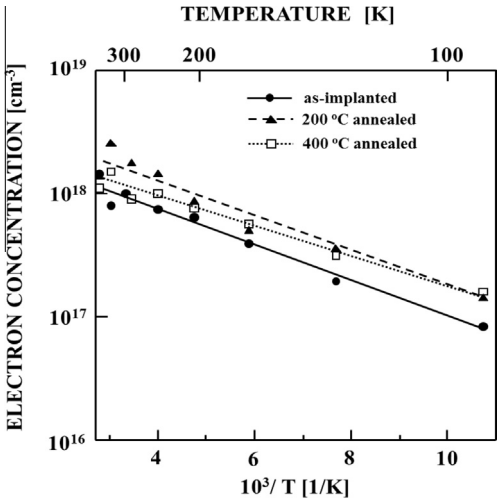

Fig. 1. Temperature dependence of electron concentration at 90–360 K of as-implanted, 200 °C, and 400 °C annealed samples.

where (dE_H/dx) is energy loss of hydrogen ion in ZnO. Since the maximum of the concentration of the implanted H is at 3600 nm in depth, the implanted H diffuses forward and backward by annealing at 200 °C and 400 °C. These ERDA measurements can evaluate the concentration of H which moved to the vicinity of the surface (surface to 300 nm or 100 nm) because of the diffusion by the annealing. Fig. 2(a) shows the hydrogen estimated from ERDA measurements for the as-implanted, 200 °C and 400 °C annealed samples. Fig. 2(b) shows hydrogen estimated using 1.5 MeV-^{4}He$^+$ beam for the 400 °C annealed samples. Compared with ERDA experiments using 2.0 MeV-^{4}He$^+$ beam, the measuring range decreased from about 300 nm for 2.0 MeV-^{4}He$^+$ beam to about 100 nm for 1.5 MeV-^{4}He$^+$ beam. It indicated that when the incident beam energy becomes small, the measuring range becomes small. In 200 °C and 400 °C annealed samples, the hydrogen yields were higher than as-implanted samples, suggesting that hydrogen was out diffused by annealing. The hydrogen yields of annealed samples were almost same. The hydrogen concentration near the surface was calculated by the following equation.

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

where Y is the yield of recoiled hydrogen near the surface, N the hydrogen concentration, Q the number of incident ^{4}He$^+$ ions (1.9×10^{13} for the present study), $(d\sigma/d\Omega)$ [6] the differential scattering cross section, $\Delta\Omega$ solid angle of detector (9.8 mrad), and θ the recoil angle (15°). From Eq. (5), the hydrogen concentration near the surface was estimated to be $\sim 3.8 \times 10^{13}$ cm^{-2} for 2.0 MeV-^{4}He$^+$ beam and $\sim 2.8 \times 10^{13}$ cm^{-2} for 1.5 MeV-^{4}He$^+$ ones.

Fig. 3 shows Electron paramagnetic resonance (EPR) in H-ion implanted ZnO. A signal with g = 1.996 was assigned to the oxygen vacancy of +charge state (V_O^+) observed in electron-irradiated ZnO [7]. In the present study, the signal of g = 1.96 would be related to V_O^+ same as the reported value (g = 1.96 [8]). This signal observed under no illumination disappeared after successive illumination with a red LED (λ = 654 nm; 1.96 eV) and appeared again with a blue LED (λ = 465 nm; 2.75 eV) illumination. One possible origin of the signal of g = 2.00 would be attributed to the defect, which may exist only near the surface [9]. Fig. 4(a) shows the energy band diagram of H implanted ZnO under no illumination. The oxygen vacancy of V_o^+ states exists at about 1 eV [10,11] below the conduction band. By the red LED illumination, electrons excited from the V_o^+ state are captured by the defect localized state (V_o^{2+}) [12] . Therefore, V_O^+ states disappear (see Fig. 4(b)) and electrons return to non-conductive states. By the blue LED illumination, electrons