Electrical and Optical Properties of ZnO Irradiated with Hydrogen Plasma

Koji Abe* and Hiroki Hata

Department of Engineering Physics, Electronics, and Mechanics, Graduate school of Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan

* Corresponding author: e-mail: abe@nitech.ac.jp

The influence of intrinsic defects and hydrogen-defect complexes on the properties of n-type ZnO crystals has been studied in terms of annealing and hydrogen plasma irradiation. Electrical and optical properties have been found to be dependent on annealing conditions and hydrogen plasma irradiation. When an as-polished sample was annealed in Ar atmosphere containing Zn vapor at 800°C for 2 h, the color of the sample changed into orange because of the formation of oxygen vacancies (V_O). In spite of the V_O formation, Hall mobility of the sample increased from 162 to 210 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Carrier concentration also increased by about four orders of magnitude. The simultaneous increases in carrier concentration and Hall mobility indicate that zinc vacancy (V_{Zn}) concentration, which acts as a compensation acceptor, are decreased by supplying Zn vapor during the annealing. Hydrogen plasma irradiation did not affect electrical properties of the sample annealed in Ar atmosphere containing Zn vapor, but improved those of the sample annealed in pure Ar atmosphere. The carrier concentration and Hall mobility increased by hydrogen plasma irradiation decreased with increasing post-annealing temperature. The post-annealing temperature dependence suggests that V_{Zn} passivated by hydrogen starts to dissociate at temperatures around 400°C.

Key words: ZnO, hydrogen, vacancy, Raman spectroscopy, carrier concentration

1. INTRODUCTION

Zinc oxide (ZnO) is a non-toxic II–VI semiconductor material with a wide bandgap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature. Because of its outstanding properties and many types of distinctive nanostructures, ZnO is considered as a promising material for various applications including light emitting diodes, ultraviolet photodetectors, transparent conductive layers, and gas sensors [1–4]. A wide range of techniques such as hydrothermal method, chemical vapor deposition (CVD), reactive plasma deposition (RPD), and aqueous solution based methods are used to synthesize ZnO [5–9]. For example, large ZnO single crystals are grown by hydrothermal method. Group III elements (B, Al, and Ga) are commonly used as shallow donors to form highly conductive ZnO films [3,7]. So far, Al- and Ga-doped ZnO films with a resistivity as low as $10^{-4} \Omega\text{cm}$ have been reported [10,11]. However, it is difficult to obtain reliable p-type ZnO. ZnO usually exhibits n-type conductivity despite acceptor doping. Intrinsic defects including oxygen vacancies (V_O), zinc interstitials (Zn_i), and zinc vacancies (V_{Zn}), which can be formed during crystal growth under non-stoichiometric conditions, are known to act as donors or acceptors [12]. Besides the group III impurities and intrinsic defects, hydrogen plays important roles in electrical conductivity of ZnO. It has been reported that hydrogen acts as shallow donors and makes hydrogen-defect complexes like VoH and $V_{Zn}H$ [12–14]. Hydrogen can be easily

incorporated into ZnO crystals because hydrogen exists in a typical crystal growth environment. In order to control the electrical conductivity, therefore, hydrogen and hydrogen-defect complexes must be taken into account. However, the knowledge about their influence on electrical properties of ZnO (carrier concentration, Hall mobility, and resistivity) is limited.

Defect concentration of a crystal generally depends on growth conditions, but intrinsic defects in ZnO are formed by electron beam irradiation and annealing. However, electron beam irradiation causes damage to both zinc and oxygen sites simultaneously. On the other hand, annealing forms an individual defect by choosing an appropriate atmosphere. The controlled formation of intrinsic defects helps to observe the influence of intrinsic defects on electrical and optical properties of ZnO. There have been a lot of studies on the properties of ZnO annealed in various conditions. Børseth et al. have reported that annealing at temperatures above 800 °C in Zn-rich and O-rich atmospheres forms V_O and V_{Zn} , respectively [15].

In this study, we have investigated the electrical and optical properties of n-type ZnO after annealing and hydrogen plasma irradiation. We discuss the influence of intrinsic defects and hydrogen-defect complexes.

2. EXPERIMENTAL

The samples used in this study were cut from a commercial ZnO crystal grown by hydrothermal method, and mechanically polished with alumina

Fig. 1. Optical transmittance spectra of the as-polished and Zn-annealed samples. The photograph shows the samples after the Ar-annealing at 800°C for 2 h (left) and Zn-annealing at 800°C for 2 h (right).

powder. The samples were cleaned with acetone in an ultrasonic bath, and rinsed in deionized water (as-polished samples). Then, the as-polished samples were annealed in pure Ar atmosphere (Ar-annealing) or Ar atmosphere containing Zn vapor (Zn-annealing). The Ar-annealing was performed at 750°C for 30 min or at 800°C for 2 h. The Zn-annealing was performed at 800°C for 2 h. In the Zn-annealing process, ZnO powder (99.999%) and carbon plates were placed on the bottom of an alumina crucible in a quartz tube furnace, and the as-polished sample was stuck on the crucible lid by carbon paste. After evacuated below 5×10^{-3} Pa, the quartz tube was filled with pure Ar. During the heating of the crucible, Zn vapor along with CO and CO₂ was supplied to the as-polished sample through the reduction of ZnO powder by carbon plates. The temperatures of the bottom and lid of the crucible were $1150 \pm 20^\circ\text{C}$ and $800 \pm 10^\circ\text{C}$, respectively. Since the surface roughness was increased by the Zn-annealing, the sample for optical transmittance measurements was mechanically polished with alumina powder. A conventional RF magnetron sputtering system was used for hydrogen plasma irradiation. The sample annealed in Ar at 750°C for 30 min was placed on a silicon wafer on the target electrode of the sputtering system and irradiated with hydrogen plasma (13.56 MHz, 100 W) at a pressure of 4 Pa for 30 min. The target electrode was water-cooled, but the sample temperature during the plasma irradiation was not controlled. After the hydrogen plasma irradiation, the sample was isochronally annealed in pure Ar at temperatures between 125 and 530°C for 30 min (post-annealing).

Optical transmittance was measured between 350 and 800 nm. Raman spectra at room temperature were obtained by using a Raman spectrometer with a 532 nm excitation laser (NRS-3300 JASCO). Resistivity and Hall effect measurements were performed at room temperature by using the van

Fig. 2. Raman spectra of the as-polished, Ar-annealed, and Zn-annealed samples. The inset shows the wide-range Raman spectrum of the as-polished sample.

der Pauw configuration. Contacts were formed by soldering indium onto the samples.

3. RESULTS AND DISCUSSION

As-polished samples were annealed in pure Ar atmosphere or Ar atmosphere containing Zn vapor at 800°C for 2 h. Optical transmittance spectra of the as-polished and Zn-annealed samples are shown in Fig. 1. The inset shows the typical photograph of the Ar-annealed and Zn-annealed samples. Although the color of the Ar-annealed sample was almost the same as that of the as-polished sample, the Zn-annealed sample exhibited coloration. The color of the sample changed into orange as previously reported [13,16]. The Zn-annealed sample showed a lower transmittance than the as-polished sample. Because of the orange coloration caused by the Zn-annealing, optical transmittance between 400 and 500 nm obviously decreased. Selim et al. have reported that V_O are responsible for the optical absorption between 400 and 500 nm [17]. The optical transmittance indicates that V_O are formed by the Zn-annealing.

Raman measurements were performed to collect more information about the formation of V_O. Because wurtzite ZnO belongs to the C_{6v} symmetry group, there are six Raman-active phonon modes, $A_1(\text{TO})$, $A_1(\text{LO})$, $E_2(\text{low})$, $E_2(\text{high})$, $E_1(\text{TO})$, and $E_1(\text{LO})$ [18,19]. The $A_1(\text{TO})$, $E_1(\text{LO})$, and $E_1(\text{TO})$ are not seen in our measurements because of the backscattering geometry [20,21]. Figure 2 shows Raman spectra obtained from the as-polished, Ar-annealed (750°C for 30 min), and Zn-annealed samples. The inset shows the wide-range Raman spectrum of the as-polished sample. There are four Raman peaks at 98, 332, 439, and 1156 cm⁻¹. The Raman peaks at 98 and 439 cm⁻¹ are assigned to the $E_2(\text{low})$ and $E_2(\text{high})$ modes, respectively [18,19]. The Raman peaks at 332 and 1156 cm⁻¹

Fig. 3. Carrier concentration and Hall mobility of the as-polished sample and the samples annealed in different conditions. A: as-polished. B: Ar-annealed at 750°C for 30 min. C: Ar-annealed at 800°C for 2 h. D: Zn-annealed at 800°C for 2 h.

are known to be the second order Raman scattering [18,20]. The Raman spectra in Fig. 2 are normalized by the intensity of the $E_2(\text{high})$ peak. In the spectrum of the Zn-annealed sample, an additional Raman peak has appeared at 581 cm^{-1} . Chen et al. reported that this broad peak in the O^+ -implanted ZnO single crystal was much smaller than that in the B^+ -implanted one [21]. This broad Raman peak at around 580 cm^{-1} has been attributed to oxygen deficiency in ZnO [21–23]. The increase of the broad Raman peak indicates that V_O was formed by the Zn-annealing. This result is consistent with the optical transmittance spectra shown in Fig. 1.

The carrier concentration and Hall mobility of the as-polished sample and those of the samples annealed in different conditions are shown in Fig. 3. The thickness of the samples A, B, C, and D were 1200, 540, 550, 750, and 550 μm , respectively. The carrier concentration and Hall mobility of the as-polished sample were $3.0 \times 10^{13} \text{ cm}^{-3}$ and $162 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. When as-polished samples were annealed in pure Ar atmosphere, carrier concentration increased and Hall mobility considerably decreased. The carrier concentration and Hall mobility of the sample after the Ar-annealing at 750°C for 30 min were $9.7 \times 10^{13} \text{ cm}^{-3}$ and $52 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. After the Ar-annealing at 800°C for 2 h, the carrier concentration and Hall mobility of the sample were $1.7 \times 10^{15} \text{ cm}^{-3}$ and $83 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. The Zn-annealing at 800°C for 2 h resulted in significant changes of the electrical properties. In spite of the formation of V_O by the Zn-annealing, carrier concentration increased to $1.9 \times 10^{17} \text{ cm}^{-3}$, and Hall mobility increased to $210 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. These values are much higher than those of the as-polished and Ar-annealed samples. It is known that V_O forms a deep donor level in ZnO and cannot contribute to the increase of carrier concentration and Hall mobility [12]. The

Fig. 4. Electrical properties of the sample irradiated with hydrogen plasma as a function of post-annealing temperature: (a) carrier concentration, (b) Hall mobility, and (c) resistivity.

simultaneous increase of carrier concentration and Hall mobility indicates that the Zn-annealing reduces the concentration of compensation acceptors. It seems that V_{Zn} concentration is decreased by supplying Zn vapor during the annealing.

In order to observe the thermal stability of the electrical properties after hydrogen plasma irradiation, the sample irradiated with hydrogen plasma was post-annealed in Ar. The Ar-annealed sample (750°C, 30 min) were irradiated with hydrogen plasma. Figures 4(a)–4(c) show electrical properties of the sample as a function of post-annealing temperature. The thickness of the sample was 860 μm . The carrier concentration and Hall mobility of the sample before post-annealing were $6.7 \times 10^{16} \text{ cm}^{-3}$ and $101 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. These values were higher than those of the sample after the Ar-annealing at 750°C for

30 min (Fig. 3). It was found that carrier concentration and Hall mobility are increased by hydrogen plasma irradiation. Electrical properties of the sample were almost unchanged by the post-annealing at temperatures below 300°C. In the range from 300 to 380°C, the carrier concentration decreased and the Hall mobility slightly increased with increasing post-annealing temperature. A further increase of post-annealing temperature significantly changed the electrical properties. Along with the simultaneous decreases in carrier concentration and Hall mobility, resistivity increased about two orders of magnitude. The carrier concentration, Hall mobility, and resistivity of the sample after the post-annealing at 530°C were $4.5 \times 10^{14} \text{ cm}^{-3}$, $74 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, and $1.9 \times 10^2 \text{ }\Omega\text{cm}$, respectively. These values were almost the same as those obtained from the sample after the Ar-annealing at 750°C for 30 min (Fig. 3). It was indicated that compensation acceptors are passivated by hydrogen and the passivated acceptors are reactivated at the temperatures around 400°C. The electrical properties of the Ar-annealed sample were improved by hydrogen plasma irradiation, while the electrical properties of the Zn-annealed sample were not affected by the hydrogen plasma irradiation. When the Zn-annealed sample was irradiated with hydrogen plasma, the carrier concentration and Hall mobility were $2.5 \times 10^{17} \text{ cm}^{-3}$ and $188 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. As discussed in Fig. 3, the Zn-annealing at 800°C for 2 h decreases the concentration of V_{Zn} . It is likely that formation and dissociation of hydrogen- V_{Zn} complexes affect carrier concentration and Hall mobility of n-type ZnO.

4. CONCLUSIONS

In conclusion, we have studied the influence of intrinsic defects and hydrogen-defect complexes on the electrical and optical properties of n-type ZnO crystals. When an as-polished sample was annealed in Ar containing Zn vapor at 800°C for 2 h, the color of the sample changed into orange. Optical transmittance and Raman measurements showed that V_{O} s were formed by the Zn-annealing. Although the concentration of V_{O} increased, electrical properties were improved by the Zn-annealing. The carrier concentration and Hall mobility of the sample were much higher than those obtained from the as-polished sample. The simultaneous increase of carrier concentration and Hall mobility indicates that the Zn-annealing reduces the concentration of V_{Zn} which acts as compensation acceptors. Hydrogen plasma irradiation did not affect the electrical properties of the Zn-annealed sample, but improved those of the Ar-annealed sample. The carrier concentration and Hall mobility of the Ar-annealed sample were simultaneously increased by hydrogen plasma irradiation, indicating that hydrogen passivates the compensation acceptors. The electrical properties improved by hydrogen plasma irradiation were stable at temperatures below 300°C. It was found that the compensation acceptors passivated by

hydrogen starts dissociating at temperatures around 400°C.

The conditions of annealing and hydrogen plasma irradiation in this study can be applied to improve electrical properties of n-type ZnO crystals.

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