Pulsed laser reactive deposition of p-type ZnO film enhanced by an electron cyclotron resonance source

Xin-Li Guo, Hitoshi Tabata*, Tomoji Kawai

Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

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Abstract

P-type ZnO films with carrier density 3–6 × 10^{18} cm^{-3}, resistivity 2–5 Ωcm and Hall mobility = 0.1–0.4 cm^{2} V^{-1} s^{-1} have been grown on fused silica and glass substrate by pulsed laser reactive deposition using a pure metal Zn target in N_{2}O plasma. The N acceptor doping was effectively enhanced using the active N formed by N_{2}O gas passing through an electron resonance source during the pulsed laser reactive deposition process. P-type conduction was achieved by optimizing the microwave-input power (E) and deposition pressure (P_{N_{2}O}). These electrical properties are sufficient for some practical applications. We expect this result to facilitate the fabrication of transparent p–n homojunctions suitable for light-emitting diodes.

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1. Introduction

ZnO is an interesting II–VI semiconductor with various electrical, optical, acoustic and chemical properties because of its wide direct bandgap of 3.3 eV at room temperature. It has been widely used in optoelectronics, sensors and catalysis [1–8]. Recently, it has attracted considerable attention as a potential candidate material for ultraviolet and blue light-emitting diodes (LEDs) [9–14]. However, the development of such optoelectronic devices has been impeded by the fact that p–n homojunctions in ZnO have been extremely difficult to fabricate. Because most of the II–VI semiconductors crystallize with a Wurtzite structure, they occur naturally as n-type semiconductors. It is, therefore, difficult to achieve p-type doping due to the “self-compensation” of shallow acceptors resulting from various intrinsic donor defects such as oxygen vacancies (V_{o}) or Zn interstitial (Zn_{i}) [11,15,16]. Despite considerable efforts, p-type ZnO has not been realized until recently through codoping methods used by Joseph et al. [12] and Minegishi et al. [13]. In both cases, N was used as a shallow acceptor and

*Corresponding author. Tel.: +81-6-6879-8446; fax: +81-6-6875-2440.
E-mail address: tabata@sanken.osaka-u.ac.jp (H. Tabata).
codoped with donor dopants Ga and Zn, respectively, to enhance the incorporation of N in p-type ZnO. However, its reproducibility is lower because of the difficulty of controlling the amounts and distribution of micro-elements doped in the ZnO films, making it unsuitable for practical application. Attempts to achieve p-type conduction using single N doping have failed due to its low solubility in ZnO and high resistivity (typically $5 \times 10^5 \Omega \text{cm}$) in fabricated p-type ZnO films [12].

In this paper, we report on our efforts to use single N doping to fabricate p-type ZnO films.

2. Experimentation

This research involved a technique called pulsed laser reactive deposition. A pure Zn metal chip ($10 \times 10 \times 1 \text{ mm}^3$) was used as the target. It was ablated by an excimer ArF laser operating at a wavelength of 193 nm, a frequency of 1–5 Hz and a fluence of approximately 1 Jcm$^{-2}$. N$_2$O plasma formed by passing through the ECR or RF source was used to enhance the oxidization of Zn and the incorporation of N in the ZnO film during the pulsed laser reactive deposition and plasma implantation process. Details of our laser deposition system featuring an electron cyclotron resonance (ECR) source have already been reported [17]. Fused silica ($15 \times 5 \times 0.5 \text{ mm}^3$) was chosen as the substrate for its compatibility with Si-based integrated circuits since an amorphous SiO$_2$ layer forms naturally on the surface of Si wafer. The glass substrate ($15 \times 5 \times 1 \text{ mm}^3$) was used for cost reasons. The deposition chamber was set at a base pressure less than $1 \times 10^{-6} \text{ mbar}$ before the deposition process was started. Films with thickness of 700–1400 nm were deposited in wide-ranging conditions of $P_{\text{N}_2\text{O}} = 1.3 \times 10^{-4}–1.0 \times 10^{-2} \text{ mbar}$, $E = 30–300 \text{ W}$ and $T_{\text{sub}} = 380^\circ\text{C}–450^\circ\text{C}$ were found to have a high $c$-axis orientation with good crystallinity (FWHM = 0.047–0.247$^\circ$). No zinc or nitride peaks were found in the XRD spectra. Because N$_2$O gas is easily dissociated, it releases oxygen atoms above 300$^\circ\text{C}$ and becomes a strong oxidizing agent during the oxide film formation. Under lower $P_{\text{N}_2\text{O}}$ ($10^{-5}–10^{-4} \text{ mbar}$) and $E$ (<30 W), the films showed poor orientation and crystallinity or amorphous growth, which is mainly caused by oxygen deficiency. The effect of $E$ on the FWHM values of XRD spectra of the ZnO films is shown in Fig. 2.

Fig. 2 shows that FWHM values of the film increase as $E$ increases when $E = 150 \text{ W}$, $P_{\text{N}_2\text{O}} = 1.8 \times 10^{-4} \text{ mbar}$ and $T_{\text{sub}} = 450^\circ\text{C}$. Conversely, the values decrease when $E > 150 \text{ W}$. At $E = 150 \text{ W}$, the film shows p-type conditions with the largest FWHM value (0.188) which might be due to N incorporation.

3. Results and discussion

3.1. X-ray diffraction

Figs. 1(a) and (b) show the typical XRD spectra of the fabricated ZnO film. All the films grown in the range of $P_{\text{N}_2\text{O}} = 1.3 \times 10^{-4}–1.0 \times 10^{-2} \text{ mbar}$, $E = 30–300 \text{ W}$ and $T_{\text{sub}} = 380^\circ\text{C}–450^\circ\text{C}$ were measured using X-ray diffraction (XRD) and atomic force microscopy (AFM).

Optical transmission spectra were measured in the visible region.

3.2. Surface morphology

The surface morphologies of the fabricated ZnO films are influenced by $E$, $P_{\text{N}_2\text{O}}$ and $T_{\text{sub}}$. The surface morphologies of ZnO films grown with various values of $P_{\text{N}_2\text{O}}$ are shown in Figs. 3(a) and (b).

The three-dimensional AFM image also indicates that the film grows along the $c$-axis orientation with high density. As $P_{\text{N}_2\text{O}}$ increases, the surface becomes rough. The values of root-mean-square roughness (rms) in Figs. 3(a) and (b) are 29 and 67 Å, respectively, for a 3.7 μm scan.
3.3. Electrical properties

The electrical properties were investigated in terms of $E$, $P_{N_2O}$ and $T_{\text{sub}}$ in the above-mentioned range. Typical results for optimizing the growth conditions for getting p-type ZnO films are shown in Fig. 4.

Fig. 4 shows that the room temperature resistivity ($\rho$) and carrier concentration ($N$) vary with $E$ at the condition of $P_{N_2O} = 1.8 \times 10^{-4}$ mbar, $T_{\text{sub}} = 450^\circ$C. When $E$ is increased to 150 W, the as-grown ZnO film shows p-type conduction ($p$) and results in $N = 5.6 \times 10^{18}$ cm$^{-3}$, $\rho = 2.1 \Omega$ cm, Hall mobility $\mu = 0.1 \times 10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$ and Hall coefficient $+ 1.1 \times 10^{-1}$ cm$^3$ C$^{-1}$. The p-type conduction cannot be achieved in ZnO film solely by oxidization [13]. Therefore, this p-type conduction is probably caused by active N forming in N$_2$O plasma which causes some sites of O atoms to be replaced by the acceptor sites in ZnO lattice. The ablated Zn atoms are fully oxidized by O. In addition, the $V_o$ and $Zn_i$ defects are either suppressed or the background electron concentration that these two defects cause is insufficient to compensate for the positive holes resulting from the N substitution in the ZnO films.

These assumptions may be realized by the following ways:

1. {	extit{Plasma implantation:}} Numerous vacancies present in the film-growing process have permitted N implantation at relatively low ECR power.
2. {	extit{Codoping:}} The incorporation of N in ZnO films can be enhanced by excess Zn under low $P_{N_2O}$, which has been identified by Minegishi et al. [13].
3. {	extit{Chemical reaction:}} A chemical reaction such as $\text{Zn} + (-\text{N-O}) \rightarrow \text{Zn-N-O}$ occurred.

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Fig. 1. XRD spectra of the ZnO/fused silica films grown at (a) $E = 150$ W, p-type ZnO, and (b) $E = 30$ W, n-type ZnO ($P_{N_2O} = 1.8 \times 10^{-4}$ mbar and $T_{\text{sub}} = 450^\circ$C).

Fig. 2. Effect of $E$ on the FWHM values of XRD spectra of ZnO films ($P_{N_2O} = 1.8 \times 10^{-4}$ mbar and $T_{\text{sub}} = 450^\circ$C).
Considering the requirements of low-temperature deposition for forming p–n junctions applicable to LEDs, we reproduced this p-type ZnO film at 380°C by increasing the ECR power around the optimized conditions to fabricate a p-type ZnO film. The electrical properties for the fabricated p-type ZnO films were in the ranges of \( N = 3 \times 6 \times 10^{18} \text{cm}^{-3} \), \( \rho = 2 \times 5 \Omega \text{cm} \) and \( \mu = 0.1 \)–0.4 cm²\text{V}^{-1}\text{s}^{-1}. High-resistance ZnO film with \( N = 1.9 \times 10^{13} \text{cm}^{-3} \) and \( \rho = 1.6 \times 10^5 \Omega \text{cm} \) was also fabricated by increasing \( P_{\text{N}_2\text{O}} \) to above 10⁻² mbar under the optimized deposition condition.

The p-type conduction has also been confirmed by simple Seebeck coefficient measurement. The resistivity of the achieved p-type ZnO using single N doping has been greatly improved from the previous value of \( 5 \times 10^5 \) to 2–5 Ω cm. Although this is still higher than donor-doped (e.g., Ga, In, Al) n-type ZnO films (about \( 10^{-4} \Omega \text{cm} \)), it is sufficient for some practical applications such as LEDs.

When \( E, P_{\text{N}_2\text{O}} \) or \( T_{\text{sub}} \) deviates from these optimized deposition conditions, the conduction inverts to n-type as indicated in Fig. 4, which reveal a sensitivity to variations in \( E, P_{\text{N}_2\text{O}} \) and \( T_{\text{sub}} \). We have not identified clear relationships between the electrical properties with the parameters of \( E, P_{\text{N}_2\text{O}} \) and \( T_{\text{sub}} \). We believe that this also implies that the electrical properties of p-type ZnO film can still be improved by further optimizing the technology process including the substrate pre-treatment, the deposition parameters, the direction of plasma implantation and the annealing treatment. More experiments will be done about this issue in our later work. The differences of electrical properties among the N-doped ZnO films and ZnO films grown in a pure-oxygen ambient (typically \( N = 1 \)–\( 7 \times 10^{17} \text{cm}^{-3} \), \( \mu = 9 \)–70 cm²\text{V}^{-1}\text{s}^{-1} \) are believed to be mainly caused by the composition effect between the hole and background carrier concentration induced by N-doping and defects in the ZnO film. The sensitivity of conduction type to \( E, P_{\text{N}_2\text{O}} \) and

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**Fig. 3.** AFM image of ZnO films: (a) \( E = 150 \text{ W}, P_{\text{N}_2\text{O}} = 1.8 \times 10^{-4} \text{mbar} \) and \( T_{\text{sub}} = 450 \text{ C}, \) p-type ZnO; (b) \( E = 150 \text{ W}, P_{\text{N}_2\text{O}} = 4.3 \times 10^{-3} \text{mbar} \) and \( T_{\text{sub}} = 450 \text{ C}, \) n-type ZnO.

**Fig. 4.** Typical electrical properties for the samples obtained in optimizing the deposition conditions in which p–n conversion has occurred (\( P_{\text{N}_2\text{O}} = 1.8 \times 10^{-4} \text{mbar} \) and \( T_{\text{sub}} = 450 \text{ C} \)).
\( T_{\text{sub}} \) may be due to the fact that \( N \) is a shallow acceptor in ZnO films and easily compensated by the background electron concentration which is sensitive to \( V_o \) and \( Z_n \). We were unable to fabricate p-type ZnO film without the enhancing of ECR source and found obvious differences between the ZnO films grown on fused silica and glass substrate.

3.4. Optical transmission spectra

Fig. 5 shows typical optical transmission spectra of p-type ZnO and n-type ZnO films measured at RT. The fundamental absorption starts at about 350 nm. The transmission of the p-type ZnO film is almost identical to that of n-type ZnO films. A large transmittance greater than 90\% is obtained in visible wavelength regions.

4. Conclusions

We have fabricated single N-doped p-type ZnO films on fused silica and glass substrate using pulsed laser reactive deposition enhanced by an ECR source. The electrical properties of the achieved p-type ZnO films are sufficient for some practical applications. Further experiments to fabricate transparent p–n homojunction thin-film diodes and to improve the electric properties are already under way.

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