Transactions of the Materials Research Society of Japan 26 [2] 465-469 (2001)

Effects of NH_3 Radical Irradiation and Excess Zn Supply on the Electric Property of ZnO Films Prepared by Ion Beam Sputtering

Takeshi Ohgaki, Naoki Ohashi*, Satoshi Wada, Isao Sakaguchi*, Hajime Haneda* and Takaaki Tsurumi
Department of Metallurgy and Ceramic Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Maguro-ku, Tokyo 152-8552, Japan.
Fax: 81-3-5734-2514, e-mail: tohgaki@crystal.ceram.titech.ac.jp
*National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

The zinc oxide (ZnO) films were epitaxially grown on sapphire substrates using ion beam sputtering process. The effects of ammonium (NH_3) radical irradiation and excess Zn supply on the electrical properties of the ZnO thin films were studied. The n-type carrier concentration was markedly reduced when Zn/ZnO composite targets consisted of Zn metal and ceramic ZnO were used with the NH_3 radical irradiation, while the irradiation of the radicals from N_2 and N_2 + H_2 gases was not effective to reduce the carrier concentration. The excess Zn supplied from the Zn/ZnO composite target evaporated during the deposition without formation of donor defects when the NH_3 radical was irradiated. The decrease in the n-type carrier concentration was attributable to the replacement of O ions in ZnO with N ions or N ions associated with hydrogen. The carrier concentration of the films prepared with NH_3 radical irradiation decreased furthermore by the annealing at 600°C in nitrogen atmosphere, which was attributable to the activation of N ion acceptors.
Key words: zinc oxide, thin films, ion beam sputtering, ammonium radicals

1. INTRODUCTION

Zinc oxide (ZnO) having a direct band gap of 3.3 eV is one of the candidates for ultraviolet optical device [1]. In order to realize opto-electronic devices using ZnO thin films, it is desirable to fabricate p-type ZnO thin films. Although various impurities, such as lithium [2], silver [3] and copper [4], have been tried to dope into ZnO films as acceptors. These acceptors yield deep levels within the band gap, so that the trapped holes cannot be ionized thermally. Kobayashi et al [5]. predicted that nitrogen (N) was a candidate for p-type dopant for producing a shallow level in ZnO due to its large electronegativety. However, the difficulty in realizing p-type ZnO had been remained, because some donor defects, such as interstitial zinc (Zn) or oxygen (O) vacancies, are formed either thermally or to compensate shallow acceptors, which is called "self-compensation".

Recently, some research groups have succeeded in preparing p-type ZnO. Butkhuzi et al. [6] reported that the p-type conduction was realized by incorporating excess oxygen into ZnO films. Joseph et al. [7] found that the N_2O radical irradiation was effective to prepare the p-type ZnO films. As for NH_3 gas, it was reported that the p-type ZnO was formed by a CVD process using the mixture of NH_3, H_2O and H_2 as a carrier gas but the process was less reproducible [8]. In GaN and ZnSe, the p-type conduction has been successfully realized using NH_3 gas. They were semi-insulators or n-type semiconductors in the as-grown state because most of shallow acceptors were compensated and passivated by H ions. To activated acceptors for p-type conduction, it was necessary to anneal in N_2 atmosphere or to be irradiated with low-energy electron beam [9-14]. It seems that the similar process with NH_3 radical irradiation is effective to activate acceptors in ZnO films. However, the effect of NH_3 radical irradiation on the structure and electric properties of ZnO thin films has not been studied yet.

The concept of NH_3 radical irradiation to dope acceptors into ZnO is that O ions in the crystal structure are first replaced with N ions associated with hydrogen (N-H ions) because N-H ions and O ions have the same valence and similar size (radius of N^{3-} in tetrahedron: 0.146 nm, N-H bond length in $NH_3(g)$: 0.101 nm and radius of O^{2-} in tetrahedron: 0.138 nm). Moreover, it appears to be difficult to replace O ions in ZnO with N-H ions because of strong Zn-O bonds. Therefore, excess Zn metal has to be supplied over oxygen during the deposition process. The ZnO films need to be annealed to activate acceptors. In this study, the ZnO films were prepared with NH_3 radical irradiation and with excess Zn supply using ion beam sputtering, and their effects on electrical properties were studied.

2. EXPERIMENTAL PROCEDURE

ZnO thin films were grown by ion beam sputtering method [15]. A schematic diagram of

the apparatus used for the growth of ZnO thin films is shown in Fig.1. The target was fixed about 100 mm below the substrate and faced to a Kaufman-type ion beam gun at an angle of 45° . During the growth of films, the thickness of the films was continuously monitored with a quartz sensor together with monitoring of the refraction high-energy electron diffraction (RHEED) patterns. A helicon plasma gun was used to irradiate the film surface with various radicals (NH_3, N_2 and N_2+H_2) during the film deposition. The flux density of radicals from the helicon plasma gun was about $1x10^{15}$ atm$\cdot$cm^{-2}s^{-1}.

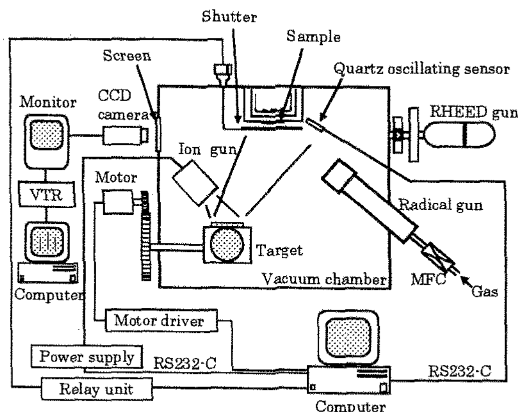


Fig.1 A schematic diagram of ion beam sputtering apparatus.

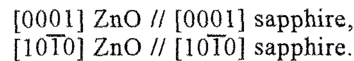
Sapphire single crystals with (0001) orientation were used as substrates. They were pretreated before the growth by ultrasonic rinsing in acetone followed by ethanol and heated at 1050 ℃ in air for 2h to make the surface atomically clean [16]. During the deposition, substrate temperature was kept at 400℃ and N_2 radical, N_2+H_2 (mixing ratio $N_2/H_2=1$) radical or NH_3 radical was irradiated. A ceramic ZnO target (99.999%) or Zn/ZnO composite targets were used for the deposition. In the composite targets, a Zn metal (99.99%) plate was placed at the center of the ceramic ZnO target. The Zn/ZnO ratio of the target was changed by the size of the Zn metal plate. The accelerating voltage of ion beam and ion beam current were 900 V and 18-22 mA, respectively. The pressure during the growth was 1.1-1.4x10^{-4} Torr. After the depositions, some of the films were annealed at 600℃ for 30 min in a nitrogen partial pressure of 3.0x10^{-5} Torr.

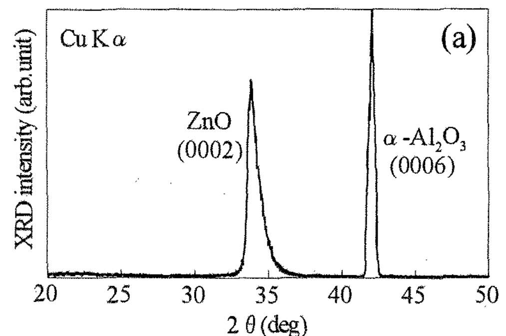
The thickness of the films was measured with a surface profiler (DEKTAK). The structure and crystallinity of the films were analyzed by X-ray diffraction (XRD) method. The electric resistivity, carrier concentration and Hall mobility of the films were determined by Hall coefficient measurement using a standard van der Pauw four-probe square geometry. Electrical contacts were made using indium ion-plating electrode, which is known to form good ohmic contact with ZnO. The N concentration in the films prepared with NH_3 radical irradiation was measured by secondary ion mass spectrometry (SIMS).

3. RESULTS AND DISCUSSION

3.1 Epitaxy of ZnO films

The thickness of all films prepared in this study was about 50 nm. Figure 2 shows a XRD profile and an RHEED pattern of a ZnO film prepared without the irradiation of radicals. Diffraction peak of ZnO (0002) and α-Al_2O_3 (0006) were observed in XRD profile. The RHEED pattern shows an assemblage of streak. These results indicate that the ZnO films are grown epitaxially on the sapphire substrates, and the surface of the films is relatively smooth. The epitaxial relation between the ZnO film and the substrate is as follows:


[0001] ZnO // [0001] sapphire,
[$10\bar{1}0$] ZnO // [$10\bar{1}0$] sapphire.



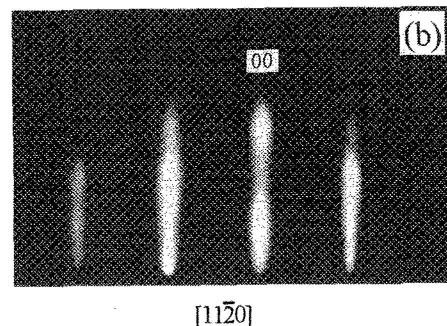


Fig.2 XRD profile (a) and RHEED pattern (b) of the ZnO film grown at 400℃.

3.2 The effects of NH_3 radical and the composite target

Table I shows electrical properties of the ZnO films prepared at 400℃ using the ceramic target or the composite targets with the irradiation of various radicals. The ratio of Zn/ZnO in the composite target was 0.1 and 0.7. The n-type carrier concentration was markedly reduced when the film was prepared using the composite target and the NH_3 radical irradiation. The carrier concentration was increased when the film was prepared without NH_3 radical irradiation. This indicated that the NH_3 radical irradiation was essential to reduce the carrier concentration.

Table I Electric properties of ZnO films prepared using ZnO target and composite target.

Target	Radical source	ρ (Ωcm)	Nh (cm^{-3})	μ ($cm^2V^{-1}s^{-1}$)
ZnO	——	8.4	$2.5x10^{17}$	3.0
	N_2	32	$4.2x10^{16}$	4.7
	N_2+H_2	8.9	$1.7x10^{17}$	4.1
	NH_3	14	$1.3x10^{17}$	3.3
Zn/ZnO=0.1	——	1.9	$1.5x10^{18}$	2.2
	N_2	21	$1.7x10^{17}$	1.7
	N_2+H_2	21	$6.8x10^{17}$	2.7
	NH_3	480	$1.3x10^{16}$	0.97
Zn/ZnO=0.7	NH_3	22000	$4.4x10^{14}$	0.64

Figures 3 and 4 show photographs and XRD profiles of the films prepared with N_2 or NH_3 radical irradiation, respectively. The film with the N_2 radical irradiation was neither homogeneous nor transparent. The intensity of the ZnO (0002) diffraction decreased with increasing Zn/ZnO without the shift of the diffraction angle. On the other hand, transparent films were obtained using the NH_3 radical irradiation. The intensity of the ZnO (0002) diffraction decreased with increasing Zn/ZnO but the shift of the diffraction angle was observed in this case. The shift of the diffraction angle indicated that the c-parameter of ZnO increased with increasing Zn/ZnO ratio. Figure 5 shows the growth rate of ZnO film at 400°C as a function of the Zn/ZnO ratio in the composite target. The growth rate decreases with increasing Zn/ZnO ratio in the target. Zn metal has a relatively high vapor pressure, therefore, the result in Fig.5 indicates that the excess Zn metal evaporated from the film during the deposition. A small portion of Zn metal reacted with NH_3 radicals and incorporated into the crystal lattice with N ions or N-H ions. The N-H or N ions replaced the O ions in the crystal lattice and acted as acceptors. The shift of the diffraction angle observed in Fig.4 may indicate the change of the lattice parameter due to the replacement. The composite target was necessary to decrease the n-type carrier concentration (Table I) because strong Zn-O bonds formed in the case of the ceramic ZnO target may prevent the reaction between Zn and NH_3 radicals.

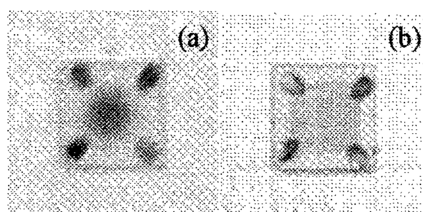


Fig.3 Photographs of the films prepared using composite target with N_2 radical irradiation (a) and NH_3 radical irradiation (b).

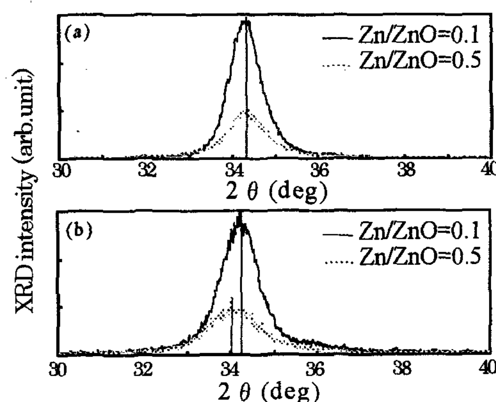


Fig.4 XRD profile of the films prepared using composite target (Zn/ZnO=0.1,0.5) with N_2 radical irradiation (a) and NH_3 radical irradiation (b).

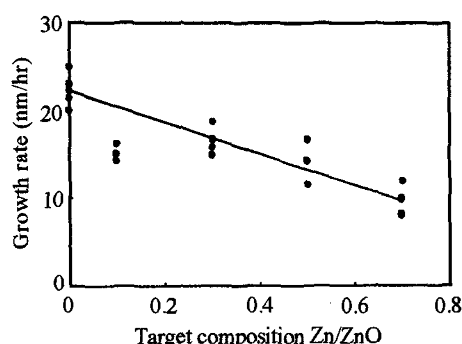


Fig.5 The relationship between growth rate and target composition Zn/ZnO at 400°C.

Figure 6 shows the change in the resistivity of the ZnO films with the RF-power of the helicon plasma gun used for producing NH_3 radicals. The Zn/ZnO ratio in the composite target was 0.7. The resistivity shows a maximum at RF-power of 20W. At higher RF-powers, N-H bonds in NH_3 radical are broken and it becomes difficult for N ions to get incorporated into the ZnO crystal. In Table I , N_2+H_2 radicals was not effective to reduce the n-type carrier concentration because N-H bond was hardly formed in N_2+H_2 radicals.

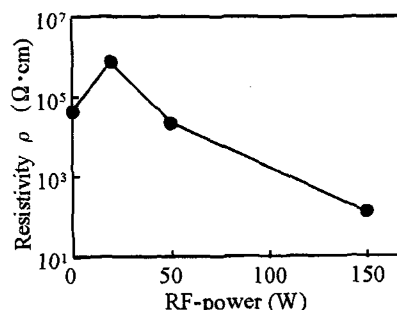


Fig.6 The relationship between resistivity and RF-power of helicon radical gun.

3.3 The effects of excess Zn supply and annealing

The relation between the carrier concentration and the Zn/ZnO ratio in the composite target is shown in Fig.7. It is obvious that the change in the carrier concentration with the Zn/ZnO ratio is larger in the case of the NH_3 radical irradiation than that of N_2 radical irradiation. The carrier concentration in the films prepared using the NH_3 radical irradiation reduced with increasing Zn/ZnO ratio. This indicates that the Zn metal in the composite target enhances the reaction with NH_3 radicals and excess Zn metal evaporates during the deposition without forming donor defects in the films. However, when the Zn/ZnO increased above 0.8, the crystallinity of films reduced markedly. The XRD profile of the poor crystalline film was that of amorphous and the film was not transparent. The results of SIMS indicated that the N concentration in the film prepared without radical irradiation was less than 10^{18} cm^{-3}, while that with NH_3 radical irradiation was 10^{19}-10^{21} cm^{-3}. Experimental results obtained in this study consistently indicate that both the NH_3 radical irradiation and the excess Zn supply are indispensable to dope N into ZnO films.

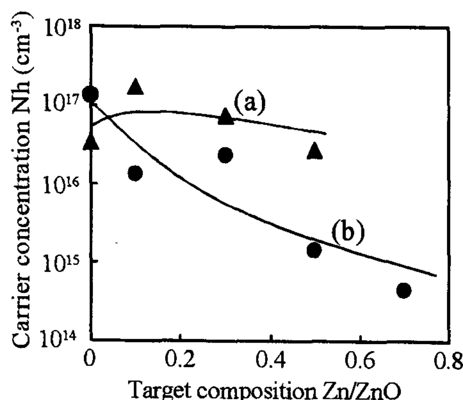


Fig.7 The relationship between the carrier concentration and the Zn/ZnO ratio in the composite target.
Closed triangles (a) show the results of the film prepared with N_2 radical irradiation and closed circles (b) show the results of the film prepared with NH_3 radical irradiation.

The ZnO films prepared with NH_3 radical irradiation were annealed in a low nitrogen pressure (3.0×10^{-5} Torr) to activate acceptors. Figure 8 shows the relation between the carrier concentration and the Zn/ZnO ratio in the composite target before and after the annealing. The n-type carrier concentration in the films prepared using ceramic ZnO target (Zn/ZnO=0) increased by the annealing. It was also observed that the carrier concentration in the films prepared with H_2, N_2 or N_2+H_2 radical irradiation was increased. In these films, N-H or N ions are hardly replaced with O ions during the deposition. Therefore, there are no acceptors to be activated and the annealing simply increases the oxygen vacancies. On the other hand, the carrier concentration in the films prepared using the composite target and NH_3 radicals decreased by the annealing. We considered that this is due to the dissociated N-H ions and activation of N ion as acceptor that was compensated and passivated by H ion in as-deposited ZnO thin films.

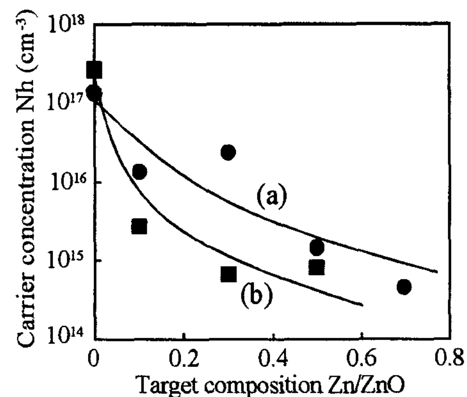


Fig.8 The relationship between the carrier concentration and the Zn/ZnO ratio in the composite target before (a) and after (b) annealing.

We have observed the decrease in the n-type carrier concentration but could not obtain p-type semiconductor. However, N-H bond of NH_3 was effective in N doping into ZnO. The NH_3 gas and activation process seems to be essential to invert conduction type.

4. SUMMARY

The effects of NH_3 radical irradiation and excess Zn supply on the electrical properties of ZnO thin films were examined. The results are summarized as follows:

1) The electrical properties of the films using ceramic ZnO target were almost independent of the N_2, N_2+H_2 and NH_3 radical irradiation.
2) The n-type carrier concentration was decreased using NH_3 radical irradiation and the excess Zn supply.
3) The excess Zn metal from the Zn/ZnO composite target evaporated during the deposition with NH_3 radical irradiation. In this case, the excess Zn hardly formed donor defects.
4) NH_3 radicals with N-H bonds and excess Zn supply were necessary to incorporate N or N-H ions in the crystal. It was considered that N-H ions could replace O ions in the ZnO because N-H ions and O ions had the same valence and similar size.
5) The carrier concentration of the films prepared with NH_3 radical irradiation decreased furthermore by the annealing at 600 ℃ in nitrogen atmosphere, which was attributable to the activation of N ion acceptors.

REFERENCES

[1] K.Minegishi, Y.Koiwai, Y.Kikuchi and Y.Yano, *Jpn.J.Appl.Phys.*, **36** L1453-L1455

(1997).
[2] A.Valentini, F.Quaranta, M.Rossi and G.Battaglin, *J.Vac.Sci. &* Technol., **A9** 286-289 (1991).
[3] Y.Kanai, *Jpn.J.Appl.Phys.*, **30** 2021-2022 (1991).
[4] Y.Kanai, *Jpn.J.Appl.Phys.*, **30** 703-707 (1991).
[5] A.Kobayashi, O.F.Sankey and J.D.Dow, *Phys.Rev.B*, **28** 946-958 (1983).
[6] T.V.Butkhuzi, A.V.Bureyev, A.N.Georgobiani, N.P.Kekelidze and T.G.Khulordave, *J.Cryst.Growth*, **117** 366-369 (1992).
[7] M.Joseph, H.Tabata and T.Kawai, *Jpn.J.Appl.Phys.*, **38** L1205-L1207 (1999).
[8] K.Minegishi, Y.Koiwai, Y.Kikuchi, K.Yano, M.Kasuga and A.Shimizu, *Jpn.J.Appl.Phys,.* **36** L1453-L1455 (1997).
[9] H.Amano, M.Kito, K.Hiramatsu and I.Akasaki, *Jpn.J.Appl.Phys.*, **28** L2112-L2144 (1989).
[10] J.A.Van Vechten, J.D.Zook, R.D.Horning and B.Goldenberg, *Jpn.J.Appl.Phys.*, **31** 3662-3663 (1992).
[11] S.Nakamura, M.Senoh and T.Mukai, *Jpn.J.Appl.Phys.*, **30** L1708-L1711 (1991).
[12] X.Li and J.J.Coleman, *Appl.Phys.Lett.*, **69** 1605-1607 (1996).
[13] K.Ogata, D.Kawaguchi, T.Kera, Sz.Fujita and Sg.Fujita, *J.Cryst.Growth*, **159** 312-316 (1996).
[14] A.Kamata, H.Mitsuhashi and H.Fujita, *Appl.Phys.Lett.*, **63** 3353-3354 (1993).
[15] T.Tsurumi, S.Nishizawa, N.Ohashi and T.Ohgaki, *Jpn.J.Appl.*, Phys. **38** 3682-3688 (1999).
[16] M.Yoshimoto, T.Maeda, T.Ohnishi, H.Koinuma, O.Ishiyama, M.Shinohara, M.Kubo, R.Miura and A.Miyamoto, *Appl.Phys.Lett.*, **67** 2615-2617 (1995).