Preparation of p-type ZnO Films by Alternate Deposition of ZnO and Mg$_3$N$_2$ Films

Kenkichiro Kobayashi$^{a,*}$, Takayuki Koyama$^a$, Xinyo Zhang$^a$, Yoshiumi Kohono$^a$, Yasumasa Tomita$^a$, Yasuhisa Maeda$^a$, and Shigenori Matsushima$^b$

$^a$Department of Materials Science, Shizuoka University, 3-5-1, Johoku, Naka-Ku, Hamamatsu, 432-8561, Japan
$^b$Department of Materials Science and Chemical Engineering, Kitakyusyu National College of Technology, 5-20-1, Shii, Kokuraminami-Ku, Kitakyushu, 802-0985, Japan

Abstract

Films were deposited on a glass substrates heated at 100 °C by alternate deposition of ZnO and Mg$_3$N$_2$ films in an atmosphere of N$_2$ + 0.2% O$_2$. p-type ZnO films with the resistivity of 9.9×10$^3$ - 4.5×10$^3$ Ωcm were grown by Mg$_3$N$_2$ sputtering for 0.2 s at 50-70 W, whereas an n-type ZnO film was grown for 0.2 s at 90 W. Appearance of the n-type ZnO film is caused by a decrease of O$_2$-partial pressure in an atmosphere. The contraction of the c-axis due to the incorporation of Mg atoms is found in these p-type and n-type ZnO films. When the Mg$_3$N$_2$-deposition period was extended to 5s, p-type ZnO films were grown in the alternate sputtering at 50 W, whereas only insulator films were grown in the alternate sputtering at 70 W. The optical band gap of the films increases with both a RF power and a period of Mg$_3$N$_2$-deposition.

© 2011 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of MRS-Taiwan

Keywords: p-type ZnO; codoping of Mg and N; alternate deposition

1. Introduction

Zinc oxide (ZnO) has attracted considerable attention from viewpoint of ultraviolet light-emitting devices (LEDs). For development of ZnO-based LEDs, the formation of pn junction is necessary. It was well known that n-type ZnO is in nature formed without intentional doping because of the presence of stable donors such as oxygen vacancies. ZnO films doped with Al and Ga atoms have been used as...
transparent electrodes [1]. In contrast, the growth of p-type ZnO films is challenging theme. The growth of p-type ZnO films has been attempted by doping of group V elements of N, P, As, and Sb [2-4]. Among group V elements, N atoms substituted for O sites behave as the most suitable acceptors. In fact, ZnO-based LEDs were fabricated by using N-doped ZnO films, but the hole-density of the N-doped ZnO film was insufficient because the concentration of N atoms was still low and the N-related acceptor levels were fairly deep [5]. In order to solve these problems, a new doping technique has been proposed theoretically. For instance, Yamamoto et al [6] proposed a codoping technique in which donors and acceptors are simultaneously incorporated such that complexes of acceptor-donor-acceptor (A-D-A) are formed. Wang et al [7] predicted that clusters of DA_n (n > 2) have more negative formation energy and their acceptor levels become shallower with the number of coordinated acceptors. Although several groups succeeded in the growth of p-type ZnO films by employing a codoping technique, there was still controversy on the reproducibility [8, 9]. Instead of a codoping technique, we have focused on δ-doping of the clusters comprising of Mg-N bonds that possess fairly shallow acceptor levels in ZnO. It was well known that δ-doping has advantages that a large number of acceptors are incorporated in a narrow region and a host material is not electrically disturbed. The purpose of this work is to prepare p-type ZnO films by employing δ-doping of Mg-N clusters. In this work, we have prepared a film by the alternate sputtering of ZnO and Mg_3N_2 targets. In the alternate sputtering, δ-doping of Mg-N clusters can be achieved by the deposition of sub-monolayer Mg_3N_2 film between ZnO films. Thus, we study electrical properties, the lattice parameters and optical properties of films prepared by varying both a radio-frequency (RF) power and a deposition period of Mg_3N_2 sputtering. On the basis of experimental data, we discuss doping mechanism in the alternate deposition. It is shown that p-type ZnO films are grown by the alternate deposition under optimal conditions of an O_2-partial pressure, a RF power and a deposition period of Mg_3N_2 sputtering.

2. Experimental

Films growth was carried out by RF-magnetron sputtering apparatus, in which ZnO and Mg_3N_2 targets were placed and a substrate holder was rotated above two targets. A chamber of the sputtering apparatus was evacuated to 1.3×10^{-4} Pa and then sputtering was performed at a pressure of 2.6 Pa in an atmospheres of N_2 + 0.2% O_2. Films were deposited on glass substrates heated at 50 - 200 °C. The alternate deposition was carried out as follows: ZnO and Mg_3N_2 targets were continuously sputtered at 30 W and 30 - 90 W, respectively. A substrate was maintained for 30 s above the ZnO target, and subsequently a substrate was moved above Mg_3N_2 target and kept for 0.2-5 s. The alternate deposition was continued up to 300 cycles. The thickness of films was measured with a surface roughness meter (Kosaka, SE-30D). The estimated film thickness was in the range of 300 to 350 nm. When a p-type ZnO film was exposed to air, its surface resistance gradually increased with time. To acquire the resistivity and Seebeck coefficient of inside a sample, a film was deposited on a glass substrate with patterned Au electrodes. The resistivity was measured by a four point probe van der pauw method. The carrier type of a film with two-prove resistance of 10^9 Ω or more was not determined from Hall-effect measurements. Alternatively, the carrier type of a film was determined by Seebeck-effect measurements. The crystal structure and the lattice parameters of films were determined by X-ray diffraction measurements in the θ-2θ scan mode using Cu Kα radiation. The composition of films was determined by X-ray photoelectron spectroscopy (XPS). Absorption spectra were taken with an UV-Vis spectrophotometer (Jasco, V-530).
3. Results and Discussion

By sputtering of Mg$_3$N$_2$ target in an atmosphere of N$_2$ + 0.2% O$_2$, Mg$_3$N$_2$ films were grown at RF powers of 70 W or more, and an amorphous film with a nominal composition MgN$_x$O$_y$ (x=0.5, y=0.25) was deposited at 50 W. Deposition rates of the films sputtered at 50 and 70 were 0.03 and 0.05 nm/s. In ZnO sputtering at 30 W, a deposition rate of an undoped ZnO film was ca. 1 nm/s. The resistivity of the undoped ZnO films was dependent on a substrate temperature. The highest resistivity was observed in an undoped ZnO film deposited at a substrate temperature of 100 °C. Accordingly, the film growth by the alternate sputtering of ZnO and Mg$_3$N$_2$ was performed at a substrate temperature of 100 °C in an atmosphere of N$_2$ + 1% O$_2$.

Figure 1 shows the relation of the resistivity of films to RF-power of Mg$_3$N$_2$-sputtering. At 30 W, the resistivity decreases slightly in comparison with that of the undoped ZnO film, but its carrier type is unclear. The films prepared by Mg$_3$N$_2$-sputtering at 50, 60 and 70 W have the resistivity of 9.9×10$^3$-4.5×10$^3$ Ωcm and show a positive Seebeck coefficient of 0.5-0.4 mV/K (p-type), respectively. The film prepared by Mg$_3$N$_2$-sputtering at 90 W exhibits a low resistivity of 1.0 Ωcm, but its carrier type is n-type. A slight change in the resistivity of the film prepared at 30W is due to insufficient supply of Mg and N atoms. Since the p-type films are grown at RF powers of 50-70 W, moderate Mg and N atoms are expected to be deposited on the ZnO film surface. The appearance of n-type film at 90 W is not related to amounts of deposited Mg and N atoms, because a deposition rate is significantly enhanced with RF power. As will be discussed later, the growth of the n-type film is ascribed to the generation of oxygen vacancies in ZnO film.

In XRD patterns of the films prepared by the alternate Mg$_3$N$_2$-sputtering for 0.2 s at RF powers of 0-90 W, there are the ZnO (002) diffraction peaks and Au (111) diffraction peaks of the Au inner electrodes. No diffraction peaks related to Mg compounds are seen in the XRD patterns. Thus, these films prepares by the alternate deposition are assigned to ZnO films containing Mg and N atoms. The c-axis of the doped ZnO films is oriented in perpendicular to the film surface. In Fig. 2, the c-axis length estimated from the ZnO (002) diffraction peak is plotted as a function of RF power of Mg$_3$N$_2$-sputtering.

![Fig. 1. Dependence of RF-power of the Mg$_3$N$_2$ target on the resistivity of films prepared by the alternate deposition of ZnO and Mg$_3$N$_2$ films in an atmosphere of N$_2$ + 0.2% O$_2$. A period of Mg$_3$N$_2$-deposition was 0.2 s. The carrier types are denoted by symbols of “p” and “n”. Symbol of “i” means that carrier type is not identified.](image1)

![Fig. 2. Dependence of RF-power of the Mg$_3$N$_2$ sputtering on c-axis length of films prepared by the alternate deposition of ZnO and Mg$_3$N$_2$ films in an atmosphere of N$_2$ + 0.2% O$_2$. A period of Mg$_3$N$_2$-deposition was 0.2 s.](image2)
The c-axis length of the undoped ZnO film is longer than that of single crystalline ZnO (c=5.207 Å). The expansion of the c-axis is due to the compression stress induced by sputtering. The further expansion of the c-axis is seen in the films prepared at 30 and 50 W. The expansion of the c-axis is not related to the compression stress induced by Mg$_3$N$_2$-sputtering, because the expansion of the c-axis was observed when a substrate was held above the ZnO target such that no Mg$_3$N$_2$ films were deposited. It was confirmed from preliminary experiments that the c-axis of an undoped ZnO film expands with a decrease of O$_2$-partial pressure in atmospheres. Accordingly, the expansion of the c-axis observed at 30 and 50 W is ascribed to the generation of oxygen vacancies in ZnO films. The decrease in O$_2$-partial pressure in an atmosphere is caused by the recombination reactions of O$_2$ with N-radicals produced in RF plasma. On the other hand, the contraction of the c-axis is seen in the films prepared at 60-90 W. The contraction is mainly ascribed to the incorporation of Mg atoms into the ZnO films (N-doping into ZnO film have little influence on the c-axis length). The incorporation of Mg and N atoms is responsible for the appearance of the p-type films prepared at 50-70 W. Nevertheless, the n-type film is grown at 90 W although large amounts of Mg and N atoms are doped into the film. In the n-type film, donors arising from oxygen vacancies prevail over the N-related acceptors.

Figure 3 shows dependence of Mg$_3$N$_2$-deposition period on the resistivity for the films prepared by Mg$_3$N$_2$-sputtering at 50 and 70 W. In sputtering of Mg$_3$N$_2$ at 50 W, all films prepared at 0.2, 2 and 5 s are p-type and the lowest resistivity of $4.5 \times 10^3$ Ωcm is achieved at Mg$_3$N$_2$-deposition period of 2 s. In Mg$_3$N$_2$-sputtering at 70 W, a film becomes p-type at Mg$_3$N$_2$-deposition of 0.2 s, but films become insulators at 2 and 5 s.

In XRD patterns of the films prepared by varying a deposition period, ZnO (002) and Au (111) diffraction peaks are seen, but diffraction peaks originating from Mg-compounds are not confirmed. In Fig. 4, the c-axis length of films is plotted as a function of Mg$_3$N$_2$-deposition period. The c-axis length for the p-type ZnO films prepared at 50 W is slightly shortened with the deposition period. The distinct contraction of the c-axis is observed for the films (5 s at 70 W). This contraction is not interpreted in terms of epitaxial growth of Mg$_3$N$_2$ films on ZnO films, because in-plane tensile strains are induced at the interface of Mg$_3$N$_2$ and ZnO films. A plausible explanation of the c-axis contraction is the diffusion of Mg and N atoms into a ZnO film with ca. 1 nm in thickness. Sputtered Mg and N atoms with a moderate kinetic energy can penetrate a thin ZnO film. It seems that intermixing of Mg$_3$N$_2$ and ZnO films occurs to some extent in the processes of the alternate sputtering.

Fig. 3. Plots of the resistivity vs. deposition period of Mg$_3$N$_2$. The carrier types are denoted by symbols of “p” and “n”. Symbol of “i” means that carrier type is not identified.

Fig. 4. Plots of the c-axis length vs. the deposition period of Mg$_3$N$_2$. The sputtering of Mg$_3$N$_2$ was carried out at 50 and 70 W.
Figure 5 shows plots of \((\alpha \omega)^2\) vs. photon energy for the films prepared by sputtering of Mg,N_2 at 50 (left) and 70 W (right). The deposition period of Mg,N_2 is varied from 0.2 to 5 s.

Figure 5 shows plots of \((\alpha \omega)^2\) vs. photon energy for the films prepared by the alternate deposition for 0.2-5 s. In sputtering of Mg,N_2 at 50 W, the optical band gap is estimated to be 3.31, 3.37 and 3.39 eV for the films prepared by Mg,N_2 deposition period of 0.2, 2 and 5 s. The optical band gap increases with a deposition period. In sputtering of Mg,N_2 at a higher 70 W, an increase of optical band gap becomes more remarkable. For instance, the optical band gap \((E_g = 3.59 \text{ eV})\) is obtained for the film prepared for 5 s. The optical band gap of an undoped ZnO film is estimated to be 3.26 eV from plots of \((\alpha \omega)^2\) vs. photon energy (results are not shown here). From the optical band gap energy, the Mg contents in ZnO films are estimated to be 5, 11 and 13% for the p-type films prepared by Mg,N_2-sputtering at 50 W for 0.2, 2 and 5 s [10]. In Mg,N_2-sputtering at 70 W, the Mg-contents are further enhanced up to 20, 22 and 33% for the films deposited for 0.2, 2 and 5 s. The Mg-contents is nearly identical with those estimated from XPS measurements, but N-contents of the films estimated from XPS measurements are about one-fifth of the Mg-contents. The low N-contents are related to low solubility of N atoms in ZnO. The Mg-content in the films deposited for 5 s is nearly identical with Mg-content estimated from its deposition rate, but a large deviation in the Mg-content is found in the films deposited for 0.2 s. The reason is that actual deposition period is larger than 0.2 s because Mg and N atoms can be deposited on the film situated far from Mg,N_2 target during the rotation of the substrate.

![Graph showing the relationship between resistivity and height of a wall for films prepared by alternate and fixed deposition methods.](image)

Fig. 6. Dependence of height of a wall on the resistivity of films prepared either by the alternate deposition of Mg,N_2 for 0.2 s or by the continuous deposition of Mg,N_2 where a substrate was fixed above the ZnO target.
In order to evaluate quantitatively the effects of the deposition of Mg and N atoms on the film situated far from Mg₃N₂ target, a wall was interposed between two targets of ZnO and Mg₃N₂. In Fig. 6, the resistivity of films is plotted as a function of the height of a wall. In Mg₃N₂-sputtering at 50 W, the resistivity of the films is almost independent of the height of walls. It should be noted that p-type ZnO films are grown by the alternate deposition irrespective of the height of walls. In contrast, n-type ZnO films are grown irrespective of the height of walls when the substrate was fixed above the ZnO target. The weak dependence of the resistivity suggests that no Mg and N atoms are supplied to the film placed above the ZnO target. Since the resistivity of the n-type films grown on the fixed substrate in the presence a wall is 4.5×10³ Ωcm, the generation of oxygen vacancies is lowered to some extent. The grown of the p-type ZnO films is attained not only by the incorporation of Mg and N atoms, but also by suppressing the generation of oxygen vacancies. The alternate deposition allows us to incorporate Mg and N atoms into ZnO films even at a small RF power where the generation of oxygen vacancies is suppressed. In Mg₃N₂-sputtering at 70 W, the presence of a wall affects the carrier types of the films. For instance, in the absence of a wall, the p-type ZnO films are grown on both rotated and fixed substrates. In the presence of walls, only the n-type ZnO films are grown whether the substrate holder was rotated or not. The alternate Mg₃N₂-deposition enhances the resistivity of the n-type ZnO film and slightly reduces the resistivity of the p-type ZnO films. The formation of the n-type ZnO films in the presence of walls is mainly ascribed to the interruption of supply of Mg and N atoms to the film that was kept above the ZnO target. It should be noted that the deposition of Mg and N atoms on the film situated far from the Mg₃N₂ target is effective to realize the p-type films, rather than the deposition Mg and N atoms on the film placed above Mg₃N₂ target.

As seen in Fig. 3, p-type ZnO films are grown by the alternate Mg₃N₂-deposition at 50 W for 0.2-5 s. In these p-type ZnO films, distinct diffusion of Mg and N atoms into ZnO films is presumed from the changes of the c-axis length. This diffusion of Mg and N atoms gives rise to the formation of N-doped Zn₁₋ₓMgxO films. Nevertheless, p-type Zn₁₋ₓMgxO films were not realized by a conventional N-doping [11]. Appearance of the p-type ZnO films is ascribed to the Mg-N clusters because the Mg-N clusters have shallower acceptor levels compared with N atoms substituted for O sites. However, it was theoretically predicted that such Mg-N clusters with positive binding energy of 0.3 eV are not spontaneously formed in the ZnO films doped with Mg and N atoms [12]. When sputtered Mg and N atoms have enough kinetic energy, large part of Mg and N atoms break into the ZnO film without the formation of Mg-N bonds. In contrast, when kinetic energy of Mg and N atoms is sufficiently low, clusters containing Mg-N bonds are formed at the ZnO surface. The latter case corresponds to δ-doping of Mg-N clusters acting as acceptors in ZnO films. Liu et al [11] succeeded in the preparation of p-type ZnMgO films, by employing δ-doping of N atoms. It is concluded that, in alternate Mg₃N₂-sputtering at 50 W, Mg and N atoms with moderate kinetic energy are in part diffused into ZnO films, and at the same time Mg-N clusters are formed on the ZnO surface.

As seen in Fig. 6, in Mg₃N₂-sputtering at 70 W, the p-type ZnO film is deposited on the substrate kept above the ZnO target. In this situation, Mg and N atoms are deposited together with the deposition of Zn and O atoms. The preparation of p-type Zn₁₋ₓMgxO films with a fairly low resistivity is not achieved by mono-doping of N atoms. Appearance of the p-type films is in connection with the formation of Mg-N clusters. As predicted theoretically, however, the formation of Mg-N clusters is difficult in the simultaneous deposition of Zn, O, Mg, and N atoms. Recent studies of sputtering indicated that clusters with large size are produced besides single atoms [13]. It was confirmed from mass spectroscopy that a large number of HfN⁺ ions were produced by sputtering HfN film. The concentration of HfN⁺ ions was one-half of that of Hf⁺ and N⁺ ions [14]. In our experiments, there is a possibility that clusters containing Mg-N bonds are produced by sputtering of Mg₃N₂ target. Mg-N clusters produced at a higher RF power of 70 W have initial high kinetic energy, but their kinetic energy is dissipated via the collision with atoms.
in atmosphere until the Mg-N clusters arrive at the surface of ZnO film situated far from the Mg$_3$N$_2$ target. Under this condition, the Mg-N clusters can be included into ZnO films without the breaking of Mg-N bonds. In the deposition above the Mg$_3$N$_2$ target, the dissipation of kinetic energy of Mg-N clusters is insufficient. As a consequence, Mg-N clusters are dissociated and subsequently Mg and N atoms are diffused into the ZnO film.

References

[1] Hao XT, Tan Li Wei, Ong K S. Zhu F. High-performance low-temperature transparent conducting aluminum-doped ZnO thin films and applications. *J Crystal Growth* 2006; 287: 44-47.

[2] Bian JM, Li XM, Zhang Y, Yu WD, Gao XD. p-type ZnO films by monodoping of nitrogen and ZnO-based p-n homojunctions. *Appl Phys Lett* 2004; 85: 4070-4072.

[3] Hwang DK, Kang SH, Lim JH, Yang EJ, Oh JY, Yang JH, Park SJ. p-ZnO/n-GaN heterostructure ZnO light-emitting diodes. *Appl Phys Lett* 2005; 86: 222101-222103.

[4] Mandalapu LJ, Xiu FX, Yang Z, Zhao DT, Liu JL. p-type behaviour from Sn-doped ZnO heterojunction photodiodes. *Appl Phys Lett* 2006; 88: 112108-112110.

[5] Tsukazaki A, Kubota M, Ohtomo A, Onuma T, Ohtani M, Ohno H, Chichibu SF, Kawasaki M. Blue light-emitting diode based on ZnO. *Jpn J Appl Phys* 2005; 44: L643-645.

[6] Yamamoto T, Yoshida H K. Solution using a codoping method to unipolarity for the fabrication of p-type ZnO. *Jpn J Appl Phys* 1999; 38: L166-169.

[7] Wang LG, Zunger A. Cluster-doping approach for wide-gap semiconductors; the case of p-type ZnO. *Phys Rev Lett* 2003; 90: 256401-256404.

[8] Joseph M, Tabata H, Kawai T. p-type electrical conduction in ZnO thin films by Ga and N codoping. *Jpn J Appl Phys* 1999; 38: L1205-1207.

[9] Zhung F, Zhu LP, Ye ZZ, Lu JG, Zhao BH, Hung JY, Wang L, Zhang ZH, Ji ZG. Effect of growth ambient on electrical properties of Al-N co-doped p-type ZnO films. *Thin Solid Films* 2005; 476: 272-275.

[10] Koike K, Hama K, Nakashima I, Takada G, Ogata K, Sata S, Inoue M, Yano M. Molecular beam epitaxial growth of wide band gap ZnMgO alloy films on (111)-oriented Si substrate toward UV-detector applications. *J Crystal Growth* 2005; 278: 288-292.

[11] Liu WW, Yao B, Li YF, Li BH, Zhang ZZ, Shan CX, Zhang JY, Shen DZ, Fan XW. p-type MgZnO thin films grown using N delta-doping by plasma-assisted molecular beam epitaxy. *J Alloys and Com* 2010; 504: 484-487.

[12] Li J, Wei SH, Li SS, Xia JB. Design of shallow acceptors in ZnO: first-principles band structure calculations. *Phys Rev B* 2006; 74: 081201-081204.

[13] Bets G, Husinsky W. Modelling of cluster emission from metal surfaces under ion impact. *Phil Trans R Soc Lond A* 2004; 362: 177-194.

[14] Kawaguchi S, Tanemura M, Tanemura S, Gotoh Y, Liao M, Shinkai S. Angular distribution of sputtered ions from HfN by Ar$^+$ ion bombardment. *Hyomen Kagaku* 2005; 26: 449-453.