Optical characterization by variable angle spectroscopic ellipsometry of nitrogen-doped

Mg_xZn_{1-x}O thin films prepared by the plasma-assisted reactive evaporation method

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Abstract

Non-doped $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films ($\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films) and nitrogen-doped $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films ($\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films) were grown epitaxially on Zn faces of ZnO single crystal substrates by the plasma-assisted reactive evaporation (PARE) method using ZnMg alloys. Optical parameters, refractive index n , extinction coefficient k , and absorption coefficient α of these films and ZnO substrate were easily estimated by variable angle spectroscopic ellipsometry. The k values of these films abruptly increased with increase in photon energy near the absorption edge region. Dispersions of n of these films were sharper with larger peak values than that of a ZnO substrate. $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown on a ZnO substrate by the PARE method are of high quality with less defects than those of a ZnO substrate. Maximum value of α of these films calculated from k was about $2 \times 10^5 \text{ cm}^{-1}$. The values of intercepts on photon energy $h\nu$ axis of $(\alpha h\nu)^2 - h\nu$ plots for these films and the ZnO substrate agree with peak energy of PL spectra, the origin of which is free excitons. These results indicate that absorption in those materials is dominated by exciton absorption.

1. Introduction

ZnO has attracted attention as a material for ultraviolet optoelectronic devices because it has a direct wide band gap energy (E_g) of 3.37 eV and exciton binding energy of 60 meV [1]. Wurtzite-type $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films also have attractive properties for optoelectronic materials to form a heterostructure or multi-quantum-well structure with ZnO. The band gap energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films may be controlled widely from 3.3 eV (ZnO) to 7.8 eV (MgO) depending on Mg composition of the films. ZnO and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films have been grown by various growth methods including molecular beam epitaxy (MBE) [2-4], pulsed laser deposition (PLD) [5, 6], metal organic chemical vapor deposition (MOCVD) [7-9] and helicon-wave-excited-plasma sputtering epitaxy [10].

We have also grown non-doped $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films ($\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films) on a ZnO (0001) single crystal substrate by the plasma-assisted reactive evaporation (PARE) method using a ZnMg alloy [11]. The PARE method was developed to grow p-type nitrogen-doped ZnO (ZnO:N) films on a ZnO substrate epitaxially [12]. These ZnO

films have high quality, and UV exciton emission was observed from homojunction diodes with a ZnO:N film/ZnO substrate structure [13].

To fabricate a heterojunction combined with a ZnO substrate and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films, it is necessary to understand the optical parameters of nitrogen-doped $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films ($\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films) grown by the PARE method. Generally, the absorption coefficient α is calculated from transmittance characteristics of the materials, and refractive index n and extinction coefficient k are calculated using reflectance spectra of the materials and Kramers-Kronig (K-K) relations [14]. However, measurement of the transmittance of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films on a ZnO single crystal substrate ($\text{Mg}_x\text{Zn}_{1-x}\text{O}$ film/ZnO substrate structure) is difficult because of the influence of strong absorption by a ZnO single crystal substrate, and it is also very difficult to calculate n and k by applying the K-K relation to reflectance spectra measured by a spectrophotometer because K-K analysis needs exact optical data over a large energy range. Spectroscopic ellipsometry (SE) is useful for studying the optical characteristics of various materials. However, surface flatness, material uniformity, and the model used

have important roles in SE. The basic model must be modified by surface roughness, grain boundary and stress of thin films. Many models modified by parameter fitting have therefore been reported. Results of SE studies on a ZnO substrate [15], ZnO films on sapphire (0001) [16, 17], sapphire (11-20) [17] and Si (100) [18], and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films on sapphire (0001) [19-22] and Si (100) [23] have been reported. However, there has been no report on the growth of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O}:\text{N}$ films on a ZnO single crystal substrate by the PARE method and analysis by variable angle spectroscopic ellipsometry (VASE).

In this study, we characterized optical parameters at the near-band edge region of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O}:\text{N}$ films grown on a ZnO substrate by the PARE method with a ZnMg alloy and ZnO single crystal substrate by using VASE.

2. Experimental details

Non-doped ZnO (0001) single crystal substrates of $10 \times 10 \times 0.5 \text{ mm}^3$ were cut from ZnO single crystals grown by the hydrothermal method (Tokyo Denpa Co., Ltd.) and

polished by chemical-mechanical polishing to obtain mirror-like surfaces.

$\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films were grown on the Zn-face of the polished ZnO substrate by the PARE method [11]. High-purity oxygen (O_2) gas (99.99995%) and ZnMg alloys (99.95%) with Mg compositions of 7.5, 15, 25 and 30 wt% were used for the starting materials of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films. Nitric oxide (NO) gas (99.7%) was also used as an acceptor dopant for deposition of $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films. Mixed vapors of Zn and Mg atoms evaporated from a crucible containing pellets of ZnMg alloy were passed through the plasma area of the oxygen gas or mixed gases of O_2 and NO excited by RF of 13.56 MHz. The substrate temperature, gas flow rates of O_2 and NO into the vacuum chamber, RF power applied to the plasma, deposition time and thicknesses of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films were 700°C, 15-20 sccm, 13 sccm and 150 W, 120-170 min and 0.25-0.32 μm , respectively (Table 1). The crystal structure of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films was characterized by X-ray diffraction (XRD) using a Philips X'pert MRD system with $\text{CuK}\alpha_1$ radiation. The surface morphology of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films was observed by an atomic force microscope (AFM) (SII, SPA-500).

Mg compositions of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films were estimated by using energy dispersive X-ray spectroscopy (ELIONIX INC., ERA-8800), and measurement was performed at 15kV. Opto-electronic properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films were also characterized by photoluminescence (PL) (Horiba Ltd., Photoluminor-U) using a diode pumped solid state laser (266 nm), reflectance spectra measured by a spectrophotometer (JASCO Co., V-550) and optical constants (n , k) measured using a VASE M-2000U system (J. A. Woollam Japan Co., Inc.). VASE measurements were performed at room temperature in the photon energy range from 1.2 to 5.0 eV with an angle of incidence Φ from 60° to 70° using a rotating analyzer ellipsometer with an auto retarder, and the data were analyzed using the Herzinger-Johs parametric dispersion model [24, 25].

3. Results and discussion

The XRD 2θ - ω scan pattern of $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown on a ZnO single crystal substrate consisted of only a wurtzite structure. Shape and full-width at

half-maximum value of these patterns were similar to those of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films grown on a ZnO single crystal substrate [11]. Fringes were clearly observed in the XRD pattern, and a smooth surface with root mean square roughness of less than 1.0 nm was observed in AFM images of $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films. These results indicate that $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown on the ZnO substrate by the PARE method have good crystallinity, flat surfaces and abrupt interfaces between $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films and ZnO substrates for VASE analysis.

Figure 1 shows values of extinction coefficient k (a) and refractive index n (b) of the ZnO substrate, $\text{Mg}_{0.07}\text{Zn}_{0.93}\text{O}$ films and $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ films as a function of photon energy $h\nu$. These graphs were obtained by applying the Herzinger-Johs parametric dispersion model to optical data of VASE. The Herzinger-Johs parametric dispersion model fitted the analysis of VASE data of the ZnO single crystal substrate, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films exactly. The k values of $\text{Mg}_{0.07}\text{Zn}_{0.93}\text{O}$ films and $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ films steeply increased with increase in photon energy near the absorption edge region and showed sharp peaks, but the k value of the ZnO substrate

gradually increased and the peak was not sharp. The peak and its value of dispersion curves of n of the $\text{Mg}_{0.07}\text{Zn}_{0.93}\text{O}$ films and $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ films were also sharper and larger than those of the ZnO substrate. Based on these results, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown on the ZnO substrate by the PARE method appear to have few defects and to be of high quality compared to the ZnO substrate, because the gradual increase of k in the absorption edge region suggests the existence of various energy levels based on defects.

PL spectra of these films and the ZnO substrate are depicted in Figure 2. Peak energy of the near band-edge (NBE) emission of ZnO substrate, $\text{Mg}_{0.07}\text{Zn}_{0.93}\text{O}$ films, and $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ films are 3.29 eV, 3.44 eV, and 3.49 eV, respectively. From temperature-dependent PL measurement (10 K to 300 K), we consider that the NBE emission of our films is free exciton (FE) emission. Neumann et al. reported that PL peaks of 3.397 eV of the $\text{Mg}_{0.06}\text{Zn}_{0.94}\text{O}$ film and 3.488 eV of the $\text{Mg}_{0.09}\text{Zn}_{0.91}\text{O}$ film grown on a c-plane sapphire substrate are FE emissions [26]. The PL intensity in the visible region, related to oxygen vacancy [27], of the $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film is weaker

than those of the ZnO substrate and the $\text{Mg}_{0.07}\text{Zn}_{0.93}\text{O}$ film. This result suggest that oxygen-related defects were filled by nitrogen, and the crystallinity was therefore improved in comparison with those of the ZnO substrate and the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films.

Figure 3 shows value of k (a) and n (b) of the ZnO substrate and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown by the PARE method using ZnMg alloys with various Mg compositions. With an increase in Mg composition x of the $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films, peaks of k and n were shifted to higher energies. The k values of all $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films steeply increased with increase in photon energy near the absorption edge region and those peaks were sharp. On the other hand, the k value of the ZnO substrate gradually increased and the peak was not sharp. Dispersions curves of n of all $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films had sharper and larger peaks than that of the ZnO substrate. These results indicate that crystallinity of $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown on the ZnO substrate by the PARE method was better than that of the ZnO substrate regardless of the quantities of N and Mg in the films.

The PL spectrum, reflectance R and k of the $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film at room temperature are shown in Figure 4. The PL emission at around 3.49 eV is FE emission.

The highest peak energy of the R spectrum corresponds to the FE emission of the PL spectrum and the k spectrum was abruptly increased near the PL peak. It is thought that R and k spectra are influenced by excitons.

Generally, the absorption coefficient α is calculated from transmittance T (%) of the material measured by a spectrophotometer from the following relation:

$$T/100 = \exp(-\alpha t),$$

where t is thickness of the material. It is difficult to characterize optical parameters of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films grown epitaxially on a ZnO substrate from transmission characteristics, because absorption of a ZnO substrate is dominant. On the other hand, α' is also calculated from k using the following relation:

$$\alpha' = 4\pi k/\lambda,$$

where λ is wavelength of light. Both α and α' are functions of λ . In the case of inter-band transition of a semiconductor with a direct transition band structure has the following relation to photon energy $h\nu$:

$$(ah\nu)^2 = A(h\nu - E_g)$$

where A is a constant. Therefore, E_g corresponds to the intercept on the $h\nu$ axis of an $(\alpha h\nu)^2 - h\nu$ plot using the absorption coefficient.

Figure 5 shows absorption coefficients of the ZnO single crystal and $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film: (a) and (b) are α' calculated from k of the ZnO substrate and the $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film, respectively. Maximum values of α' of the ZnO single crystal substrate and $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ films were $1.9 \times 10^5 \text{ cm}^{-1}$ and $2.1 \times 10^5 \text{ cm}^{-1}$, respectively.

Figure 6 shows an $(\alpha' h\nu)^2 - h\nu$ plot using absorption coefficient α' and PL spectrum of the ZnO substrate and also an $(\alpha' h\nu)^2 - h\nu$ plot using α' and PL spectrum of the $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film. The $(\alpha' h\nu)^2 - h\nu$ plot using α' calculated from k of the ZnO substrate increases steeply with increase in photon energy $h\nu$, and the intercept of the tangent line ($E_{\alpha'}$) is about 3.27 eV, almost corresponding to PL peak energy. The $(\alpha' h\nu)^2 - h\nu$ plot of the $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film using α' calculated from k increases abruptly with increase in photon energy $h\nu$, and the intercept of the tangent line is about 3.48 eV, almost corresponding to the PL peak of the $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film. These values also almost correspond to the peak energy of dispersion curves of refractive index n as

shown in Figure 1.

Figure 7 shows the relations of Mg composition x with PL peak energy and E_g value of $\text{Mg}_x\text{Zn}_{1-x}\text{O}:\text{N}$ films and a ZnO single crystal. The energy (E_R) of a large peak with the highest energy of reflectance spectra of these samples is also shown. PL peak energy, E_g and E_R values of each sample were almost the same and increased with increase in x of $\text{Mg}_x\text{Zn}_{1-x}\text{O}:\text{N}$ films. However, these values do not correspond to inter-band gap E_g of these materials because of binding energy of the excitons. Again, PL peak energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O}:\text{N}$ films grown on a c-plane sapphire by plasma-assisted molecular beam epitaxy [28] and band gap value estimated by the absorption coefficient α of $\text{Mg}_x\text{Zn}_{1-x}\text{O}:\text{N}$ films grown on a quartz substrate by RF plasma-beam assisted pulsed laser deposition [29] were also plotted in Figure 7. These plots are slightly lower than our values.

In our previous study [11], we estimated band gap of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films using energy of a small peak that appeared in the tail of the higher energy side of a large peak with the highest energy of reflectance spectra. However, in this study, it was difficult to

identify this small peak for $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films, because it was not clear as shown in Figure 4. Therefore, energy of a large peak with the highest energy of the reflectance spectrum was used as clear value obtained from reflectance spectra. As shown in Figure 7, since the energy of the large peak corresponds to PL peak energy, it is thought that the large peak is related to free excitons. The small peak that is thought to be related to inter-band gap E_g of $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films may be covered in the tail of the large peak of the reflectance spectrum. These results indicate that absorption at the NBE region in these materials is dominated by exciton absorption. VASE with the Herzinger-Johs parametric dispersion model was useful for determining the optical parameters n , k and absorption coefficient of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films on ZnO substrates and of a thick ZnO substrate without the influence of absorption of the ZnO substrate.

4. Conclusion

$\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films were grown epitaxially on single crystal ZnO (0001) substrates by the PARE method using ZnMg alloys as source materials. Optical constants n and k of a ZnO single crystal substrate, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films

and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown on a ZnO single crystal substrate were easily calculated by VASE without the influence of absorption of the ZnO substrate. The k values of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films abruptly increased with increase in photon energy near the absorption edge region and showed sharp peaks, but that of a ZnO substrate gradually increased and the peak was not sharp. Dispersions of n of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films were sharper with larger peak values than that of a ZnO substrate. It was cleared from VASE analysis that $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown on a ZnO substrate by the PARE method are of high quality with less defects than those of a ZnO substrate. Maximum value of the absorption coefficient α' of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films calculated from k was about $2 \times 10^5 \text{ cm}^{-1}$. The values of intercepts on the $h\nu$ axis of $(\alpha'h\nu)^2 - h\nu$ plots for the ZnO substrate, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films corresponded to energies of the free excitons but did not correspond to inter-band gaps of these materials. These results indicate that absorption at the NBE region in those materials is dominated by exciton absorption. The VASE method with the Herzinger-Johs parametric dispersion model

was useful for determining optical constants and absorption coefficient and for evaluating crystal quality of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown on a ZnO single crystal substrate.

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Table caption

Table1. Experimental conditions of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films (a) - (d) and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films (e) - (h).

Figure Captions

Figure 1. Extinction coefficients k (a) and dispersion curves of refractive index n (b) of a ZnO single crystal substrate, $\text{Mg}_{0.07}\text{Zn}_{0.93}\text{O}$ film and $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film obtained by applying the Herzinger-Johs parametric dispersion model to optical data of VASE.

Figure 2. PL spectra of an $\text{Mg}_{0.07}\text{Zn}_{0.93}\text{O}$ film, an $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film and ZnO substrate.

Figure 3. Extinction coefficient k (a) and dispersion curves of refractive index n (b) of the ZnO substrate and $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films with different Mg compositions obtained by applying the Herzinger-Johs parametric dispersion model to optical data of VASE.

Figure 4. Extinction coefficient k , reflectance R and PL spectrum of $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ films at 300 K.

Figure 5. Absorption coefficients α' calculated from k of the ZnO single crystal (a) and the $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film (b).

Figure 6. $(\alpha' h\nu)^2 - h\nu$ plots and PL spectra of the ZnO substrate and the $\text{Mg}_{0.08}\text{Zn}_{0.92}\text{O:N}$ film at room temperature. α' was calculated from k .

Figure 7. Relationships between Mg composition x and PL peak energy (gray circle), $E_{\alpha'}$ (black square) and E_R (open rhombus) values of $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films and ZnO single

crystal at room temperature. A black triangle shows PL peak energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown on a c-plane sapphire substrate [28] and an open triangle shows E_g calculated from the absorption coefficient α of $\text{Mg}_x\text{Zn}_{1-x}\text{O:N}$ films grown on a quartz-glass substrate [29].

Table 1

Sample	Substrate	RF	O ₂ gas	NO	Deposition	Film	Mg
	temperature	power	flow	gas	time	thickness	composition
	(°C)	(W)	rate	flow	(min)	(μm)	x
			(sccm)	rate			
				(sccm)			
(a)	700	150	20	-	120	0.32	0.02
(b)	700	150	20	-	130	0.32	0.03
(c)	700	150	20	-	140	0.28	0.07
(d)	700	150	20	-	150	0.26	0.13
(e)	700	150	15	13	120	0.30	0.02
(f)	700	150	15	13	130	0.30	0.04
(g)	700	150	15	13	160	0.27	0.08
(h)	700	150	15	13	170	0.25	0.15

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7