Structural and optical properties of ZnMgO thin films grown by pulsed laser deposition using ZnO-MgO multiple targets

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Abstract. We report on structural and optical properties for Zn$_{1-x}$Mg$_x$O (ZMO) thin films produced by pulsed laser ablation. ZMO thin films were grown on a-plane Al$_2$O$_3$ substrates at 400°C. In order to efficiently incorporate Mg into ZnO thin films, we used multiple ZnO-MgO ablation targets. Pulses from a Nd:YAG laser (4th harmonic generation: 266 nm) were directed on the ZnO-MgO ablation targets, which consisted of MgO single crystals mounted on ZnO ceramic targets. The ZMO films were characterized by x-ray diffraction, optical transmittance and cathodoluminescence (CL) measurements. Highly c-axis oriented ZMO(0002) reflections corresponding to the wurtzite-phase were observed. The c-axis lattice constants of the films were determined from the ZnMgO(0002) peak. The c-axis length of the ZMO films decreased linearly with Mg content. From the optical transmittance spectra of ZMO films, we observed a blue shift in the absorption edge with increasing Mg content. Band gap energies of ZMO thin films were determined from the optical transmittance and CL spectra. We found that the band gap energy changed from 3.27 eV to 3.95 eV. The Mg content of ZMO films increased monotonically with the number of laser pulses which struck the MgO target. These results show that laser ablation using multiple targets of ZnO and MgO is effective for band engineering of ZMO.

1. Introduction
Laser ablation techniques have been widely used in various applications of material processing and surface modification. In addition, pulsed laser deposition (PLD) has been found to be a stable technique for thin film growth of a variety of materials, such as oxides and high-Tc superconductors. The II-VI material zinc oxide (ZnO) has direct wide band gap energy of 3.3 eV at room temperature and a large exciton binding energy of 60 meV. Zinc oxide and its ternary oxide alloys show great promise for applications in UV photon emitters and detectors, spin functional devices, gas sensors, transparent electronic devices, and surface acoustic wave devices [1-4]. For band gap engineering of these ZnO alloys, one of the candidate materials is magnesium oxide (MgO). Several techniques have been reported for the preparation of thin films of ZnO and Zn$_{1-x}$Mg$_x$O (ZMO) by using PLD [5], plasma-assisted molecular beam epitaxy (MBE) [6], metal-organic chemical vapor deposition (MOCVD) [7], and sputtering [8]. Films of single-phase and epitaxial ZMO alloys having a band gap greater than 5.0 eV have been realized by PLD [9]. Recently, ZMO ternary alloys with a band gap of ~6.0 eV have also been fabricated by using multilayer deposition of ZnO/MgO layers [10]. Stable ZMO alloys with a well controlled energy band gap are required for device applications such as UV sensors. In this paper, we report on structural and optical properties for ZMO thin films produced by pulsed laser ablation using multiple ZnO-MgO targets.
2. Experimental
Thin films of ZMO were fabricated on single-crystal a-plane Al₂O₃ substrates using a Nd:YAG laser (266 nm, 4th harmonic). The laser beam was concentrated with a focusing lens. The energy density and pulse repetition rate of the laser were 1-2 J/cm² and 10Hz, respectively. The target-substrate distance was 35 mm. The deposition was conducted at a substrate temperature of 400 °C in 400 mTorr of oxygen atmosphere, and the growth rate was 150 nm/h. In order to efficiently incorporate Mg into ZnO thin films, we used multiple ZnO-MgO ablation targets as shown in Fig. 1. The ablation targets consisted of ZnO ceramic (99.999% purity) and single crystal MgO. When a non-doped ZnO thin film was produced, the MgO single crystal substrate was not put on the ZnO ceramic target. On the other hand, the MgO single crystal was placed on the ZnO ceramic target according to the amount of Mg required for the ZMO thin films. Pulse laser number ratio, \( n \) was given by the irradiation ratio of pulse number of ZnO and MgO, \( N_{\text{ZnO}} \) and \( N_{\text{MgO}} \), respectively. By controlling the pulse number ratio of applied laser pulses, it is possible to control the incorporation of Mg into the ZnO thin films. Similar work has been reported on a series of epitaxial ZnMgO films of varied composition by using combinatorial laser molecular beam epitaxy [11][12]. Our methodological difference in these combinatorial techniques is to perform the ablation continuously without switching the target.

The effects of Mg incorporation into ZMO thin films on the crystalline and optical characterization were characterized using x-ray diffraction (XRD) measurements, transmittance and absorption spectra, and cathodeluminescence (CL) measurements.

![Fabrication procedure of ZMO using ZnO-MgO multiple targets](image)

3. Results and discussion
X-ray diffraction patterns from the ZMO films grown on a-plane sapphire substrates by using ZnO-MgO multiple targets are shown in Fig. 2, in which the result for ZnO is also shown for comparison. Highly oriented c-axis ZMO(0002) reflections corresponding to wurtzite-phase (WZ) and single-phase ZnMgO were observed for all the samples; these films grew epitaxially as single phase crystals on Al₂O₃ substrates without any evident rocksalt (RS) phase. As shown in Fig.2 (a), the ZMO(0002) peaks were shifted to higher angles, and the ZMO(0002) peak position gradually increased with increasing Mg incorporation, as given by the change in the irradiation ratio of the ablation target. While the Mg concentration predicted by the irradiation ratio differed from the actual Mg content in the films, it was possible to control the latter by varying the irradiation ratio of the ablation targets. We take the laser pulse number ratio \( n \) as an indicator of Mg content for ZMO, and calculate c-axis lattice constants from the XRD pattern. The c-axis lattice constants were determined from the (0002) diffraction peaks. The c-axis values were estimated to change from 0.520 to 0.513 nm compared with 0.520 nm for a hexagonal ZnO. The c-axis lattice constants of ZMO films decreased with increasing the Mg content. This observed reduction was considered to be due to Mg incorporation. The calculated lattice parameter is consistent with ZMO alloys previously fabricated by PLD [5]. Our results showing a tendency of decreasing c-axis length are in good agreement with those observed by other fabrication techniques [13].
Optical properties of ZMO thin films were observed to be influenced by variation of the irradiation ratio between ZnO and MgO ablation targets. The transmittance spectra of ZMO films with different Mg content are shown in Fig.3. Highly transparent thin films were obtained with spectra that indicate optical transparency over 85%. Shifts of the absorption edge to higher photon energy were observed with increasing Mg content. Figure 4 shows absorption spectra calculated from transmittance spectra and CL spectra measured at 300 K for the ZMO thin films fabricated by using the ZnO-MgO multiple targets. The band-gap energy, \( E_g \), was calculated from a plot of \( \alpha \) versus \( E_g \) by assuming a \( \alpha(h\nu) \propto (h\nu - E_g)^2 \) relationship, where \( \alpha \) is the absorption coefficient and \( h\nu \) is the photon energy. From this plot, \( E_g \) of the ZMO were changed from 3.27 eV to 3.95 eV. It is evident from the data that up to 0.7 eV in band gap off-set can be realized in ZMO-based heterostructures. The major CL peak from non-doped ZnO was observed at 3.298 eV, and the CL peak energy was also shifted towards the higher energy side with increasing Mg content.

Next, we summarize the band gap energy obtained by absorption and CL data. Figure 5 shows the dependence of the band gap energy on the content of ZMO alloys grown by using ZnO-MgO multiple targets where the content is determined by the laser pulses ratio into the MgO target. Good agreement was found between the absorption edge and CL peak energy. Here, we considered that the Mg content in a film is proportional to laser pulse number ratio, \( n \). Although it is difficult to compare with our previous results obtained by using ZMO bulk targets [14], if one considers that the composition of the target is equivalent, the prior results agree with those reported here. In general, the band gap energy of the ternary ZMO alloy is given as follows [15]:

\[
E_g = \frac{n \cdot (3.27 eV) + (1-n) \cdot (3.95 eV)}{1}
\]
Photon energy \([eV]\)  
Absorption edge  
CL peak energy  
ZnMgO bulk target \([14]\)  
ZnO-MgO multiple target  
300 K  
Pulse number ratio, \(n\) = \(\frac{N_{\text{MgO}}}{N_{\text{ZnO}}+N_{\text{MgO}}}\) \([\%\]  

\[
E_g (\text{Zn}_{1-x} \text{Mg}_x \text{O}) = (1-x) E_g (\text{ZnO}) + xE_g (\text{MgO})
\]  

(1)

The band gap energy is assumed to be linearly dependent on Mg content. In this case, the Mg content given as a function of \(n\) was gradually increased in samples with band gap energies of 3.27 eV to 3.95 eV. The Mg content in ZMO films obtained using multiple targets was lower than that of films fabricated by ZnMgO bulk targets. Since the absorption coefficient of MgO is small, the ablation of MgO does not seem to be done more easily than that of ZnO; however, the advantage of the PLD technique using multiple targets lies in the ability to control the composition of the thin films.

4. Summary

High quality Zn\(_{1-x}\)Mg\(_x\)O (ZMO) thin films with well controlled band gap energies were produced by using multiple targets of ZnO and MgO. Structural and optical properties for ZMO thin films were measured. The c-axis lattice constant of the ZMO films was found to decrease with increasing numbers of pulse number ratio. Due to the Mg content in ZMO films, transmittance spectra and CL spectra were blue-shifted, and we found that the band gap energy changed from 3.27 eV to 3.95 eV. The Mg content of ZMO films increased monotonically with the pulse number ratio which struck the MgO target. These results suggest that laser ablation by using multiple ZnO-MgO ablation targets is effective for band gap engineering of ZMO films.

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