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Enhanced second-harmonic generation in $Mg_{0.05}Zn_{0.95}O/Mg_{0.4}Zn_{0.6}O$ multilayers

C.Y. Liu[a,b,*], B.P. Zhang[a,c], N.T. Binh[a], K. Wakatsuki[a,c], Y. Segawa[a,c]

[a]*Photodynamics Research Center, RIKEN (The Institute of Physics and Chemical Research), 519-1399 Aoba, Aramaki, Aoba-ku, Sendai 980-0845, Japan*

[b]*Department of Physics, Tonghua Teachers College, Tonghua, Jilin, China*

[c]*Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*

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Abstract

Second-harmonic generation (SHG) from a $Mg_{0.05}Zn_{0.95}O/Mg_{0.4}Zn_{0.6}O$ multilayers fabricated by the metalorganic chemical vapor deposition (MOCVD) technique was carried out. By comparing the second-harmonic signal generated in three kinds of sample, ZnO, $Mg_{0.4}Zn_{0.6}O$ film and $Mg_{0.05}Zn_{0.95}O/Mg_{0.4}Zn_{0.6}O$ multilayers, deposited at the same temperature and having almost the same thickness, we concluded that a significant enhancement of the second-harmonic signal can be achieved in $Mg_{0.05}Zn_{0.95}O/Mg_{0.4}Zn_{0.6}O$ multilayers. The second-order susceptibility tensor $\chi^{(2)}_{zzz}$=21.2 pm/V was deduced from a multilayer structure deposited at 300 °C with a total thickness of ~1 μm, which is about two times greater than that of ZnO and $Mg_{0.4}Zn_{0.6}O$ films.

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1. Introduction

Wide-bandgap semiconductors are attracting much attention because of the increasing need for short-wavelength photonic devices and high-power, high-frequency electronic devices. Remarkable progress has been achieved in semiconductor GaAs, ZnSe, SiC, GaN and ZnO-related materials [1,2]. These efforts have resulted in the demonstration of room temperature blue and green laser diodes [3,4]. In integrated optical fields, it is necessary to develop new nonlinear optical materials with larger nonlinear optical coefficients and small sizes. Many studies have been carried out on nonlinear optical waveguides made of $LiNbO_3$, $LiTaO_3$, and $KTiOPO_4$ [5,6]. However, expensive single crystals are required for fabricating them. Also, the integration ability is limited. Therefore, the development of a new material with a large nonlinear optics response and small size that can be integrated for application is needed. Recently, II–VI semiconductor material ZnO has been widely investigated in many fields from film growth to various optical properties [7,8]. Like GaN, ZnO has a wide bandgap energy of 3.37 eV and a high excition binding (60 meV) at room temperature. Its thermal conductivity and thermoelectric constant are 0.006 cal K/cm and 12 000 mV/K, respectively. These high values give ZnO strong resistance to high temperature electronic degradation during operation. The extremely high melting point of around 2300 K suggests that the optical damage threshold of ZnO may be higher than those of many common nonlinear optical materials. It is regarded as a good candidate material for green, blue or shorter wavelength light emitting diodes. Nonlinear optical effects, for example, second-harmonic generation (SHG) and third-harmonic generation of ZnO thin films have been reported [9–11]. It has been reported that the bandgap of ZnO could be widened up

* Corresponding author. Photodynamics Research Center, RIKEN (The Institute of Physics and Chemical Research), 519-1399 Aoba, Aramaki, Aoba-ku, Sendai 980-0845, Japan. Tel.: +81 222282012; fax: +81 222282010.
E-mail address: cyliu@postman.riken.go.jp (C.Y. Liu).

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to ~4.0 eV by forming a ternary alloy of MgZnO [12]. The lattice constants of MgZnO did not change significantly compared to those of ZnO because of the similar ion radius between Zn^{2+} and Mg^{2+}. Even when the Mg concentration was increased up to ~36%, the ternary alloy had a hexagonal structure. Various methods can be used to grow MgZnO film. The optical properties of MgZnO structures have been investigated [13]. Some nonlinear optical effects have been extensively investigated in a III–V narrow band-gap ternary alloy semiconductor. However, there are very few reports about a ternary alloy of MgZnO.

In this paper, we report SHG measurements on MgZnO multilayers deposited on a sapphire substrate by metal-organic chemical vapor deposition (MOCVD). For comparison, MgZnO and ZnO thin films were also deposited at the same conditions. It was found the SHG signal of a $Mg_{0.05}Zn_{0.95}O/Mg_{0.4}Zn_{0.6}O$ multilayers was larger than those of the others. For a film with thickness of ~1 μm, second-order susceptibility tensor $\chi^{(2)}_{zzz}$=21.2 pm/V was obtained, the value being about two times greater than that obtained from ZnO and $Mg_{0.4}Zn_{0.6}O$ films.

2. Film fabrication and characterization

All of the films ($Mg_{0.05}Zn_{0.95}O/Mg_{0.4}Zn_{0.6}O$ multilayers, $Mg_{0.4}Zn_{0.6}O$ and ZnO films) were grown on Al_2O_3 ($11\bar{2}0$) substrates by MOCVD. The $Mg_{0.05}Zn_{0.95}O/Mg_{0.4}Zn_{0.6}O$ multilayers were grown on a thin $Mg_{0.07}Zn_{0.93}O$ buffer layer and consist of 10 periods of alternating 50-nm $Mg_{0.4}Zn_{0.6}O$ and 45-nm $Mg_{0.05}Zn_{0.95}O$ layers. Oxygen gas, diethyl zinc ($Zn(C_2H_5)_2$, DEZn) and bismethyl cyclopentadienyl magnesium ($Mg(CH_3C_5H_4)_2$, $(MeCp)_2Mg$) were used as precursors and nitrogen was used a carrier gas for DEZn and $(MeCp)_2Mg$. Oxygen was introduced into the growth chamber and the pressure was controlled at 0.8×10^3 Pa. When the substrate temperature was increased to the growth temperature (300 °C), Zn and Mg precursors were introduced into the chamber. During growth, the flow of O_2 was set to be 10 sccm and that of N_2 was adjusted to control the Mg composition. The temperatures of DEZn and $(MeCp)_2Mg$ were 4 and 172 °C, respectively. A ternary MgZnO layer and a binary ZnO layer were prepared under similar conditions. The Mg composition and thickness of the ternary MgZnO alloy layer were 0.4 and ~1 μm, respectively. A four-crystal X-ray diffraction machine was used to characterize the crystalline quality, by measuring the rocking curve, and to determine the epitaxial relationship, by measuring the Φ scan.

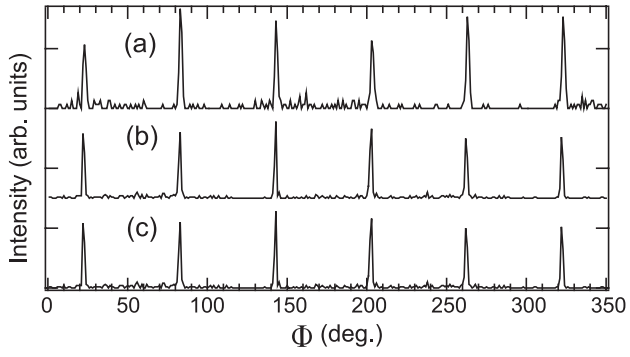

Fig. 1. Φ scans of the $\{11\bar{2}2\}$family of planes of (a) ZnO film, (b) $Mg_{0.4}Zn_{0.6}O$ layer and (c) $Mg_{0.05}Zn_{0.95}O/Mg_{0.4}Zn_{0.6}O$ multilayers.

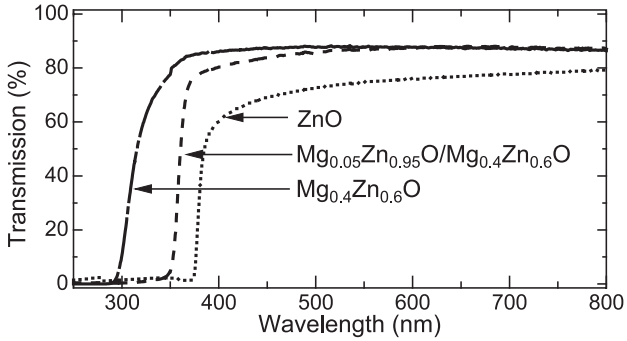

Fig. 2. Room temperature transmission of ZnO, $Mg_{0.05}Zn_{0.95}O/Mg_{0.4}Zn_{0.6}O$ and $Mg_{0.4}Zn_{0.6}O$ films.

Fig. 1 shows Φ scans of the $\{11\bar{2}2\}$ planes of different samples. Six-fold symmetry was obtained from all of the samples, unambiguously demonstrating that the samples were grown epitaxially. Our results indicate that epitaxial growth of films can be obtained for three kinds of film. The thickness of the films was ~1 μm measured by ALPHA STEP 500. The transmission spectra were measured and are shown in Fig. 2.

3. Second-harmonic generation

The experiment was set up as normal transmission mode. The 1.06 μm output of a Q-switched Nd:YAG laser (pulse width of 15 ns, repetition rate of 50 Hz) was used as the fundamental beam. In order to minimize the influence of fundamental beam power fluctuation, the fundamental beam was split into two parts. One was used as a reference beam and passed through a Y-cut quartz plate (1 mm) and the other passed through the samples. The SHG signal was collected by a quartz lens (focal length of 20 cm) and was redirected into a spectrometer connected to a charge coupled device for spectra measurement. The intensities of SHG signals from reference and sample were measured by two indentical photomultiplier (FACT 50) tubes and then averaged by an oscilloscope (Tektronix, TDS 3054 B). The intensity of the SHG signal from the sample was normalized by that from the quartz plate and then the fluctuation of the fundamental beam was eliminated. In order to increase the fundamental beam intensity, a quartz lens with a focal length of 50 cm was used to focus the beam moderately. To prevent damage to the sample, the films were placed slightly away from the focus point where the transverse spot size was ~1 mm. The film was mounted on a step-motorized rotating stage so that