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Cubic $Mg_xZn_{1-x}O$ films grown on SiO_2 substrates

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Abstract

Cubic $Mg_xZn_{1-x}O$ thin films were deposited on amorphous silicon dioxide substrate by reactive electron beam evaporation (REBE) at low temperature (250 °C). The characterizations of crystalline structure and morphology of the ternary films demonstrated that the cubic $Mg_xZn_{1-x}O$ films are of highly (001) orientation and have uniform surface. The cubic $Mg_{0.83}Zn_{0.17}O$ film deposited on quartz demonstrates wide band gap (6.45 eV) and has very high transparency (>95%) in broad wavelength range from ultraviolet (0.3 μm) to mid-infrared light (5.5 μm). The refractive indices for the cubic $Mg_xZn_{1-x}O$ decrease as Mg fraction increases. The characters of low optical absorption in broad wavelength range and feasibility of changing refractive index by Mg fraction variation in the ternary $Mg_xZn_{1-x}O$ films could render potential applications in integrated optical devices.

Keywords: Cubic $Mg_xZn_{1-x}O$ thin films; Structural properties; Optical properties

1. Introduction

Zinc oxide (ZnO) thin films have been used as transparent conducting films for opto-electronic devices, such as solar cells [1], liquid crystal display [2], and heat mirrors [3]. ZnO is also used as optical material for application in integrated optical devices, such as planar optical wave-guides [4–7]. However, in the application of ZnO to the integrated optical devices, there is difficulty in the fabrication of ZnO single-mode wave-guides. Because ZnO is normally deposited onto amorphous substrates such as fused quartz, glass or oxidized silicon, the high refractive contrast between such substrates and ZnO film implies very small channel dimensions (less than 500 nm) for single-mode operation [8]. ZnO optical wave-guide structure fabricated on Si or SiO_2/Si substrates showed high optical loss, such as 1–3 dB/cm with ZnO films grown by r.f. planar magnetron sputtering methods [7,8] and by chemical bath deposition (CBD) onto soda lime glass [9]. The primary reason of high optical loss for ZnO waveguides could be due to the band gap of ZnO being not wide enough and free carrier absorption because ZnO is a semiconductor.

$Mg_xZn_{1-x}O$ alloys are solid solution consisting of different fraction of ZnO and MgO. $Mg_xZn_{1-x}O$ alloys have two different crystal structures with Mg composition variation from 0 to 1, i.e., the hexagonal phase (the ZnO-like Wurtzite structure) with low Mg composition (<0.33) [10], and the cubic phase (the MgO-like NaCl structure) with high Mg composition ($\geqslant$0.51) [11]. In 1998, Ohtomo et al. reported the synthesis of the hexagonal $Mg_xZn_{1-x}O$ films on sapphire by pulsed laser deposition (PLD) [10]. Later in 2002, Choopun et al. prepared the cubic $Mg_xZn_{1-x}O$ films on sapphire and MgO substrates by PLD [12]. In 2003, Qiu et al. realized cubic $Mg_xZn_{1-x}O$ ($x \geqslant 0.51$) thin films on

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silicon substrates at low temperature [13]. Cubic $Mg_xZn_{1-x}O$ renders different physical properties compared to hexagonal ZnO, such as wider band gap that can be tailored by changing the Mg fraction. Band gap as high as 5.0–6.7 eV of cubic $Mg_xZn_{1-x}O$ has been realized by changing the fraction of Mg [11,12]. The wider band gap of the cubic $Mg_xZn_{1-x}O$ presumably has lower optical absorption than that of ZnO.

Refractive index is one of the important optical properties of the $Mg_xZn_{1-x}O$ film alloys. The refractive indices for hexagonal $Mg_xZn_{1-x}O$ epitaxial films ($x = 0.00, 0.24, 0.36$) were measured by a prism-coupling technique using rutile prism [14]. It should be noted that the refractive indices of hexagonal $Mg_xZn_{1-x}O$ decrease with the increasing of fraction of Mg in the films. Thus it is expected the refractive indices for cubic $Mg_xZn_{1-x}O$ can be changed by variation of Mg composition as well.

In this paper cubic $Mg_xZn_{1-x}O$ thin films were grown on amorphous silicon dioxide (SiO_2) substrate by reactive electron beam evaporation (REBE) at low temperature. The crystalline structure and optical properties for the ternary thin films that is to be applied in integrated optical devices are investigated.

2. Experiments

Cubic $Mg_xZn_{1-x}O$ films were deposited on SiO_2/Si(001) and double-side polished quartz substrates by low temperature deposition technique [13]. Prior to deposition, SiO_2/Si(001) substrates were cleaned in de-ionized water by ultrasonic, then bathed (100 °C) in de-ionized (DI) water for 10 min, and dried using nitrogen gas. The reason of SiO_2/Si(001) directly bathed in DI water is that Si was cleaned before high temperature oxidation. Quartz substrates were bathed in Na_2CO_3 solution at 100 °C for 15 min, then rinsed in DI water and finally dried using nitrogen-gas. High-purity polycrystalline $(MgO)_y(ZnO)_{1-y}$ (with the purity of 99.99%) targets were used as the evaporation sources. All the samples were grown at the substrate temperature of 250 °C. High purity oxygen gas was introduced in the growth chamber during deposition and working vapor pressure is 3×10^{-4} Torr. The concentrations of Mg in the thin films were measured by PLA-SPECI inductively coupled plasma (ICP). Characters of the interfaces of thin films and morphology of the surface were measured by scanning electron microscopy (SEM). X-ray diffraction (XRD) was measured by a D/max-ra diffraction to determine the crystalline structure. Optical characters were analyzed by transmission spectra by using Shimadzu UV-240 spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The refractive indices of cubic $Mg_xZn_{1-x}O$ alloys were obtained from calculating interference peaks of transmission spectra by Manifacier method [15].

3. Result and discussion

The morphological characters of the $Mg_{0.83}Zn_{0.17}O$ epitaxial films were obtained with scanning electron microscope (SEM). An SEM image for cubic $Mg_{0.83}Zn_{0.17}O$ grown on SiO_2/Si(001) substrate is shown Fig. 1. As can be seen, the interfaces of SiO_2/Si, SiO_2/$Mg_{0.83}Zn_{0.17}O$ were distinguished clearly. Thickness of $Mg_{0.83}Zn_{0.17}O$ film with 300 nm is determined from SEM magnification of the specimen cross-section cleavage. Moreover, crystal grains are compact and surface is uniform, and no cracking lines are observed. SiO_2 layer with thickness of about 70 nm can be seen between $Mg_{0.83}Zn_{0.17}O$ thin film and Si substrate, which was obtained by high temperature oxidation. Cubic $Mg_{0.83}Zn_{0.17}O$ thin film covers the SiO_2 layer homogenously. Further deposition experiments showed that cubic $Mg_{0.83}Zn_{0.17}O$ thin films with the thickness of exceeding 2 μm also had uniform surface and did not cracks either, in contrast to ZnO thin films grown on Si or SiO_2 substrates, in which dense cracking lines were observed when the thickness of ZnO film exceeds about 1 μm. It is attributed to the soft nature of ionic character of the alloys due to Mg–O ionic bond and low energy oxide–oxide interface between SiO_2 substrate and the $Mg_xZn_{1-x}O$ films. Thus cubic $Mg_{0.83}Zn_{0.17}O$ thin films grown on SiO_2/Si(001) and quartz substrates take on good crystal quality.

X-ray diffraction (XRD) was carried out to study the properties of crystalline structure of the $Mg_{0.83}Zn_{0.17}O$ thin films. Fig. 2 represents XRD patterns of the $Mg_{0.83}Zn_{0.17}O$ grown on SiO_2/Si(001) and quartz substrates. Curve (a) corresponds to the $Mg_{0.83}Zn_{0.17}O$ film grown on SiO_2/Si(001) substrates and curve (b) is from the $Mg_{0.83}Zn_{0.17}O$ film grown on double-side polished quartz substrates. It is seen that (002) diffraction peak of the $Mg_{0.83}Zn_{0.17}O$ films dominates both of the XRD curves, which indicates that the crystalline phase of the deposited $Mg_{0.83}Zn_{0.17}O$ thin films on both of SiO_2/Si(001) and quartz substrates are cubic. And the films are highly (001) oriented. Except for the (002)

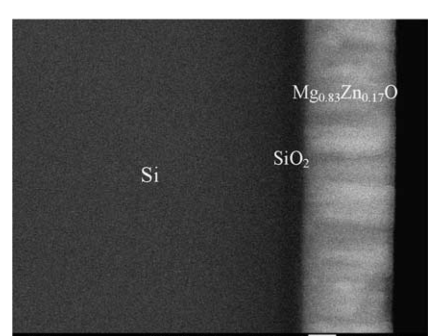

Fig. 1. A cross-sectional SEM image of cubic $Mg_{0.83}Zn_{0.17}O$ thin films deposited on SiO_2/Si(001) substrate.

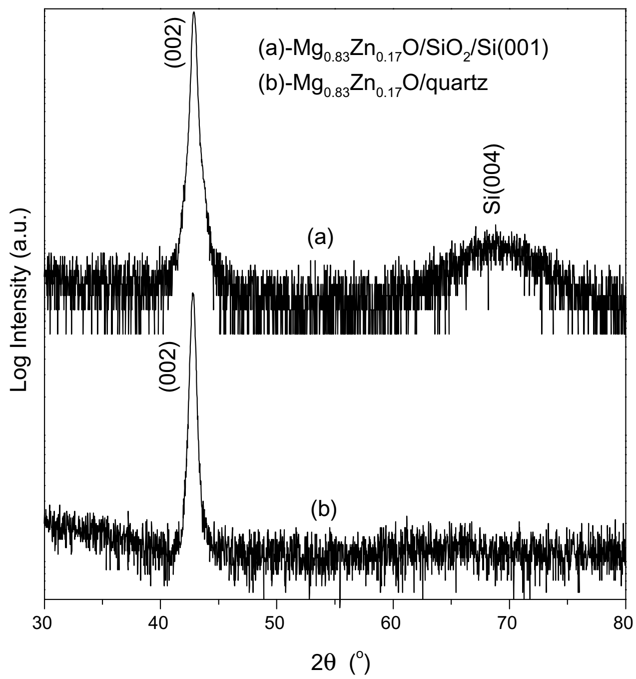

Fig. 2. XRD patterns of cubic $Mg_{0.83}Zn_{0.17}O$ thin films grown on different substrates: (a) SiO_2/Si(001); (b) quartz.

dominant peak from the epitaxial film, a weak (004) diffraction peak from Si substrate is also observed. The width of the substrate peak is large. The reason is that two thick layers with the 1.9 μm of SiO_2 and 2.0 μm of cubic $Mg_{0.83}Zn_{0.17}O$ successively cover on the Si(001) substrate in this sample. Thus, when X-ray is incident onto $Mg_{0.83}Zn_{0.17}O$ thin film and SiO_2 layer, it is diffracted and absorbed by both of the epitaxial films, and the intensity of X-ray that penetrates into the Si substrates is very weak. Consequently, the diffraction from the Si(001) substrates is weak. For the $Mg_{0.83}Zn_{0.17}O$ film grown on quartz substrate, only $Mg_{0.83}Zn_{0.17}O$ (002) diffraction peak is detected and the intensity of the peak is high, indicating high (001) orientation of the cubic $Mg_{0.83}Zn_{0.17}O$ film deposited on quartz substrate as well. Diffractions from SiO_2 were not observed from Fig. 2(a) and (b), because SiO_2 has amorphous structure.

The characters of optical absorption and refractive index were analyzed using transmission spectra of cubic $Mg_xZn_{1-x}O$ thin films on double-side polished quartz. Fig. 3 presents an optical transmission spectrum of cubic $Mg_{0.83}Zn_{0.17}O$ film (0.5 μm) on quartz substrate, with wavelength range from ultraviolet to visible light (190 nm–900 nm). For comparison, a transmission spectrum of hexagonal ZnO film (2.4 μm) grown on quartz is also plotted in the figure. The band gap energies for ZnO and $Mg_{0.83}Zn_{0.17}O$ were determined by theoretical simulation to the optical transmission spectra (Fig. 4). In the simulation intrinsic square-root absorption and the Urbach exponential absorption are included. The details of

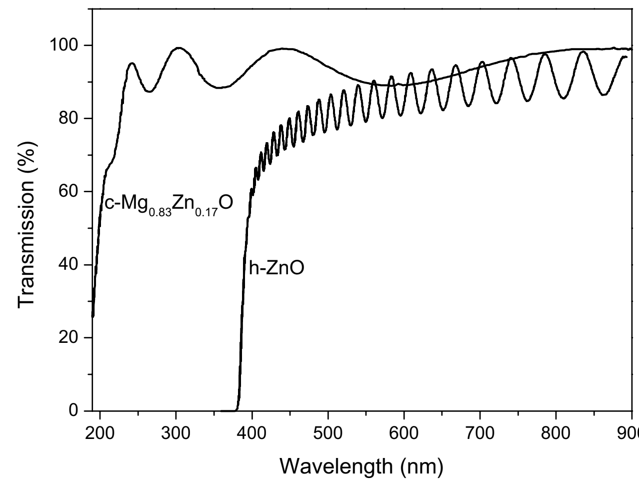

Fig. 3. Transmission spectra of cubic $Mg_{0.83}Zn_{0.17}O$ and hexagonal ZnO grown on quartz substrates.

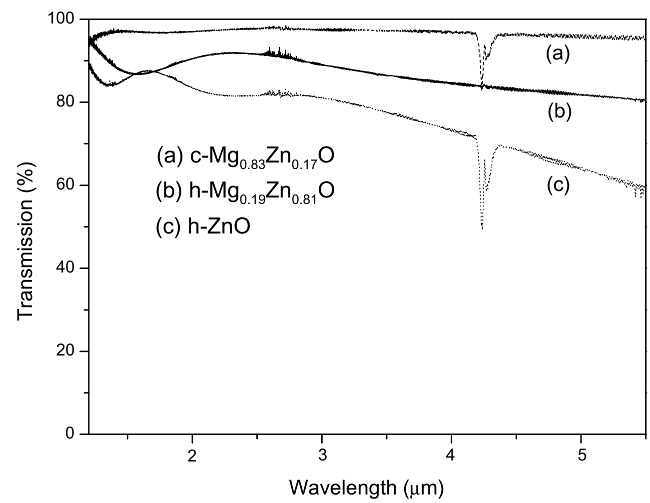

Fig. 4. Infrared transmission spectra of thin films on SiO_2 substrates: (a) c-$Mg_{0.83}Zn_{0.17}O$; (b) h-$Mg_{0.19}Zn_{0.81}O$; (c) h-ZnO.

the method were described in Ref. [11]. Band-gap energy for the cubic $Mg_{0.83}Zn_{0.17}O$ thin films is 6.45 eV, while ZnO has band gap of 3.33 eV. Obviously, the cubic $Mg_{0.83}Zn_{0.17}O$ has much wider band gap than that of ZnO. From the transmission spectra, it is seen that cubic $Mg_{0.83}Zn_{0.17}O$ shows high transparency in the measured wavelength range (300–900 nm). It can be concluded that the optical loss of the $Mg_{0.83}Zn_{0.17}O$ film due to absorption and scattering is lower than ZnO. Modulation phenomenon displayed in the Fig. 3 is due to thin film interference effect.

The optical transmittances for $Mg_xZn_{1-x}O$ ($x = 0.00, 0.19, 0.83$) films in the infrared wavelength range of 1.0–5.5 μm are shown in Fig. 5. It demonstrates that cubic $Mg_{0.83}Zn_{0.17}O$ film (0.5 μm) also has highest transmittances (>95%) in the infrared wavelength. As wavelength increases from 1.5 to 5.5 μm the transmittance

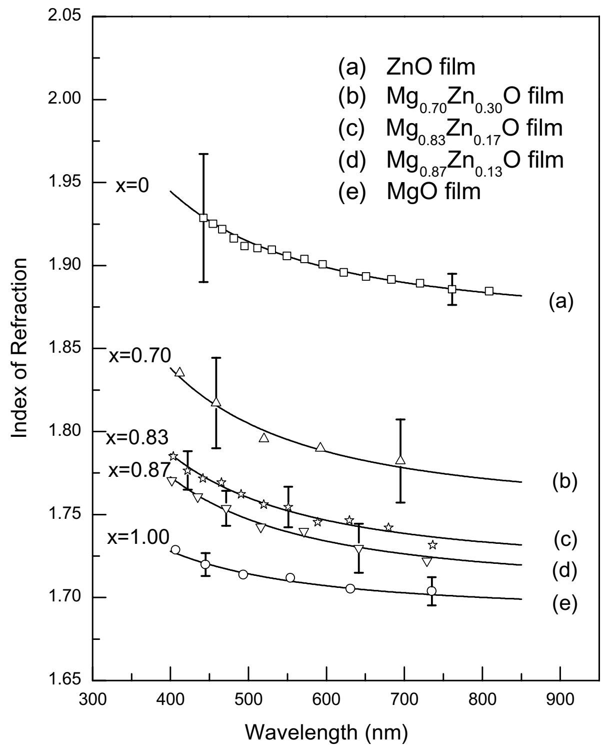

Fig. 5. Refractive indices of $Mg_xZn_{1-x}O$ ($x = 0.00, 0.70, 0.83, 0.87, 1.00$) thin films: (a) ZnO; (b) $x = 0.70$; (c) $x = 0.83$; (d) $x = 0.87$; (e) MgO.

almost keep constant, while the transmittances of hexagonal $Mg_{0.19}Zn_{0.81}O$ film (0.60 μm) and ZnO film (0.72 μm) go down quickly. The decrease magnitude of transmittance for the hexagonal $Mg_{0.19}Zn_{0.81}O$ film is slower than that of ZnO film. It indicates that when light propagates in the wave-guides made of ZnO film the attenuation will be higher than that of hexagonal $Mg_{0.19}Zn_{0.81}O$ and cubic $Mg_{0.83}Zn_{0.17}O$ film. It can be concluded that the optical losses decrease with the increase of Mg composition in the ternary $Mg_xZn_{1-x}O$ alloy films. The phenomenon of optical absorption at ~4.2 μm is due to the absorption of CO_2 because the measurement was carried out in atmosphere.

The refractive indices of the cubic $Mg_xZn_{1-x}O$ films with high-Mg concentration varying from 0.55 to 1.0 were obtained by the transmission measurements and Manifacier calculation method. The detailed description of the optical interference method and the precision of the refractive index determination are published in Ref. [16]. The index dispersions for the $Mg_xZn_{1-x}O$ ($x = 0.00, 0.70, 0.83, 0.87, 1.00$) films as a function of wavelength are shown in Fig. 5. It is seen that in the visible light region of 400–800 nm, it follows the first-order Sellmeier dispersion equation and decreases with the increase of the Mg fraction. The refractive index decreases from 1.94 to 1.73 at the wavelength of 400 nm when x increases from 0.00 to 1.00. The refractive index of ZnO obtained here is slightly smaller than that of ZnO grown using PLD technique by Teng et al. [14]. The higher refractive index of ZnO in Ref. [14] can be attributed to the higher density of oxygen vacancies involved, because the substrate temperature of ZnO grown by PLD is much higher (~600 °C) and ZnO crystallinity grown at high temperature is prone to be rich of metallic Zn. The refractive indices of the cubic $Mg_xZn_{1-x}O$ ($0.55 \leqslant x \leqslant 1.0$) is between the indices of ZnO and MgO, which is higher than the refractive index of amorphous SiO_2 ($n = 1.46$ at $\lambda = 633$ nm). The feasibility of refractive index variation by changing Mg fraction in the ternary $Mg_xZn_{1-x}O$ films renders potential applications in opto-electronic devices such as optical waveguides.

4. Conclusion

Cubic $Mg_xZn_{1-x}O$ thin films were deposited on amorphous silicon dioxide substrates (SiO_2/Si(001) and quartz) at 250 °C by REBE. The characterizations of crystalline structure and morphology of the ternary films demonstrated that the cubic $Mg_xZn_{1-x}O$ films are of highly (001) orientation and have uniform surface. The band gap of cubic $Mg_{0.83}Zn_{0.17}O$ film deposited on quartz was determined to be 6.45 eV by optical transmission measurement and theoretical simulation, which is much higher than 3.33 eV of ZnO. It has very high transparency (>95%) in broad wavelength range from ultraviolet (0.3 μm) to mid-infrared light (5.5 μm). The refractive indices for the cubic $Mg_xZn_{1-x}O$ decreases as Mg fraction increases. Compared to ZnO binary material, the ternary $Mg_xZn_{1-x}O$ has the advantages of having lower optical absorption and feasibility of changing its refractive index by Mg fraction variation in the ternary films. These characters could render its potential applications in integrated optical devices.

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