Preparation of p-type ZnMgO thin films by Sb doping method

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Abstract
We report on Sb-doped p-type $Zn_{0.95}Mg_{0.05}O$ thin films grown by pulsed laser deposition. The Sb-doped $Zn_{0.95}Mg_{0.05}O$ films show an acceptable p-type conductivity with a resistivity of $126\,\Omega$ cm, a Hall mobility of $1.71\,cm^2\,V^{-1}\,s^{-1}$ and a hole concentration of $2.90 \times 10^{16}\,cm^{-3}$ at room temperature. Secondary ion mass spectroscopy confirms that Sb has been incorporated into the $Zn_{0.95}Mg_{0.05}O$ films. Guided by x-ray photoemission spectroscopy analysis and a model for large-size-mismatched group-V dopants in ZnO, an $Sb_{Zn}-2V_{Zn}$ complex is believed to be the most possible acceptor in the Sb-doped p-type $Zn_{0.95}Mg_{0.05}O$ thin films.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO, with a direct bandgap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, is presently receiving worldwide attention because of its advantages for short-wavelength optoelectronic devices [1, 2]. It is well known that the bandgap of ZnO can be widened by doping with MgO. Also, the ionic radius of Mg^{2+} (0.57 Å) is close to that of Zn^{2+} (0.60 Å). Therefore, ZnMgO is a suitable material for quantum confinement structures from the viewpoint of bandgap engineering [3]. However, realization of p-type ZnO and p-type ZnMgO is difficult due to the asymmetric doping limitations [4]. Thanks to considerable worldwide efforts, the recent breakthrough in p-type doping has made the applications of ZnO material more feasible [5–8]. In this regard, similar efforts to dope ZnMgO thin films are strongly demanded. On the other hand, the investigations on p-type ZnMgO films are currently limited. P-doped p-type ZnMgO fabricated by pulsed laser deposition (PLD) [9] and Al–N co-doped p-type ZnMgO fabricated by ultrasonic spray pyrolysis (USP) [10] have been reported. Recently, the synthesis of p-type $Zn_{1-x}Mg_xO$ films by means of Sb doping has also been demonstrated

[11]. However, the p-type doping mechanism is not well understood, especially for Sb doping. For device fabrication, a better understanding of doping behaviour in p-type ZnMgO is required. In this work, we investigate p-type behaviour in Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin films grown by PLD. The tailored properties of the films are readily presented.

2. Experimental details

Sb-doped $Zn_{0.95}Mg_{0.05}O$ films were prepared on glass substrates by the PLD method. The substrates were cleaned with alcohol for 30 min and then rinsed in de-ionized water before being loaded into the chamber. The target was high-purity $ZnO–MgO–Sb_2O_3$ ceramic disc with a Mg content of 5 at% and a Sb content of 2.96 at%. A KrF excimer laser (Compex102, 248 nm, 25 ns) was employed as the ablation source. The laser repetition rate was 3 Hz and the energy per pulse was 300 mJ. The distance between the target and the substrate was 4.5 cm. The vacuum chamber was evacuated to a base pressure of 4×10^{-4} Pa and then high-purity O_2 (99.999%) was introduced. The growth pressure was 0.7 Pa. All the films were deposited at 400 °C for 45 min.

The electrical properties of the films were examined by Hall-effect measurements using the van der Pauw

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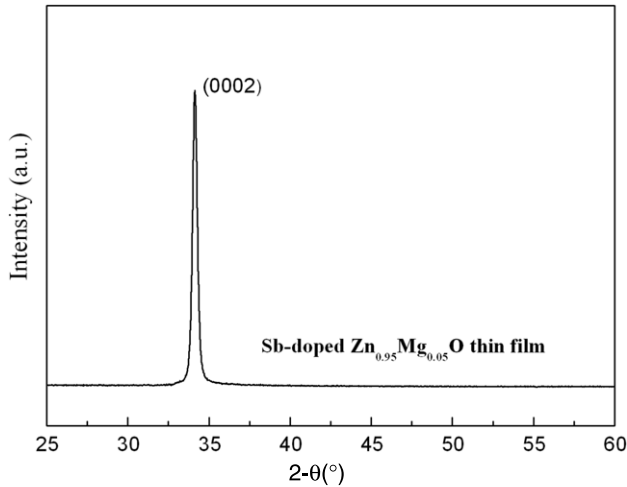[4] Author to whom any correspondence should be addressed.

Figure 1. XRD pattern of Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film deposited on glass substrate at 400 °C.

configuration (BIO-RAD HL5500PC) at room temperature. X-ray diffraction (XRD) analysis was performed on a Bede D1 system with Cu $K\alpha$ radiation (λ = 0.154 06 nm). The depth profile of Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film was measured by secondary ion mass spectroscopy (SIMS) (Cameca IMS-3f). Photoluminescence (PL) measurements were performed at room temperature on a Fluorolog-3-Tau fluorescence spectrometer. The chemical bonding states of Mg and Sb were analysed by x-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250, Al $K\alpha$ radiation source $h\nu$ = 1486.6 eV).

3. Results and discussion

The average thickness of the films is approximately 300 nm measured by cross-sectional scanning electron microscopy (FEI Sirion 200 FEG SEM). Figure 1 shows the XRD pattern of the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film. Only a peak corresponding to the ZnO (0 0 0 2) plane is observed, and no diffraction from other phases such as Sb_2O_3 or MgO is detected. It is suggested that the film is of acceptable crystallinity with a high preferential c-axis orientation.

For comparison, a Sb-doped ZnO thin film was also prepared. The deposition process was exactly the same as that of the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film except that a high-purity ZnO–Sb_2O_3 ceramic disc with Sb content of 2.96 at% was used for the Sb-doped ZnO thin film. Table 1 summarizes the electrical properties of the Sb-doped ZnO and Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin films at room temperature. To examine the reliability of the results, Hall-effect measurements were repeated four times and similar results were obtained. The Sb-doped ZnO thin film exhibits p-type conductivity, but obviously worse than that of the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film. For the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film, a resistivity of 126 Ω cm, a Hall mobility of 1.71 $cm^2\,V^{-1}\,s^{-1}$ and a hole concentration of $2.90 \times 10^{16}\,cm^{-3}$ were acquired. The results may be understood as follows. Observation of p-type conductivity in Sb-doped ZnO films indicates the formation of an acceptor state by Sb doping. At the same time, the addition of Mg can move the conduction band edge up in

Table 1. Electrical properties of Sb-doped ZnO and Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin films deposited on glass substrates at 400 °C.

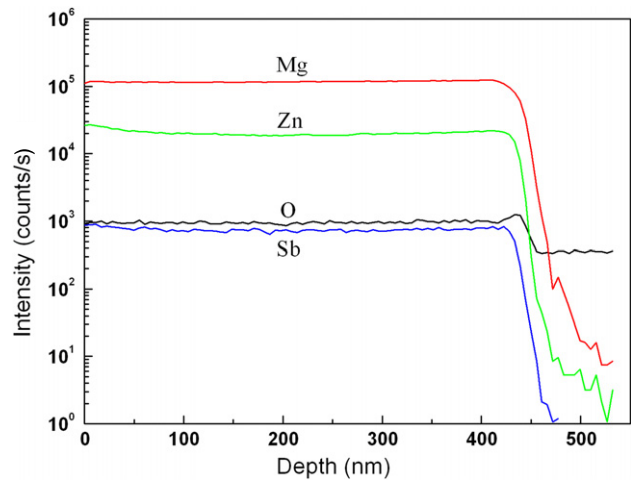| Sample	Resistivity (Ω cm)	Hall mobility ($cm^2\,V^{-1}s^{-1}$)	Carrier concentration (cm^{-3})	Carrier type
ZnO	620	0.437	2.30×10^{16}	p
$Zn_{0.95}Mg_{0.05}O$	126	1.71	2.90×10^{16}	p
ZnMgO (30 days later)	151	2.25	1.83×10^{16}	p

Figure 2. SIMS depth profile of the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film.

energy and potentially away from the intrinsic shallow donor state, thus increasing the activation energy of the defect donors and reducing the background electron concentration [12]. Therefore, it is possible that the better electrical properties of the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film are attributed to the incorporation of Mg, which will reduce the background electron concentration. To investigate the stability of the p-type conductivity, Hall-effect measurements were performed again 30 days later. It is found that the Sb-doped p-type $Zn_{0.95}Mg_{0.05}O$ thin films still keep the p-type conductivity without any obvious degradation.

In order to investigate the element composition distribution in the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film, a depth profile was carried out by SIMS measurements, as shown in figure 2. Quantitative results could not be obtained due to the lack of reference samples for the SIMS measurement. The contents of Zn, Mg and O keep constant throughout the whole film. Also, Sb has been well detected, uniformly distributed in the film, which is responsible for the p-type conductivity.

PL measurements were performed to characterize the optical properties of the Sb-doped ZnO and the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin films. The room-temperature PL spectra are presented in figure 3. The Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film as well as the Sb-doped ZnO thin film exhibits a peak located in the UV region, which originates from the excitonic near-band-gap emission. The emission of Sb-doped $Zn_{0.95}Mg_{0.05}O$ is located at 3.48 eV, showing a blueshift compared with that of Sb-doped ZnO (3.23 eV). This blueshift is believed to be the result of the incorporation of Mg. The comparative PL spectra suggest that Mg doping contributes to the bandgap widening in the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film.

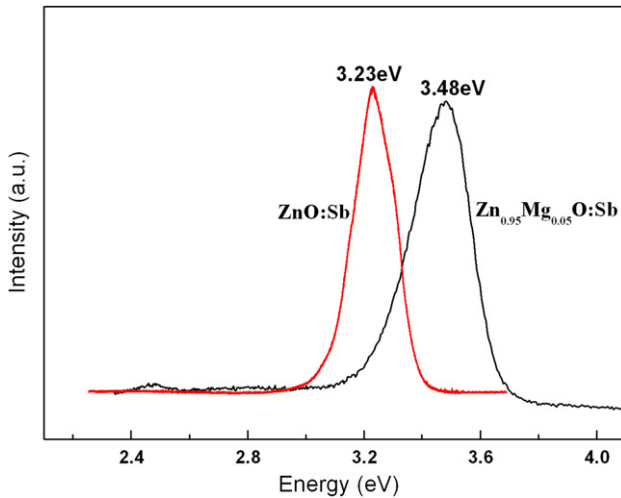**Figure 3.** Room-temperature PL spectra of Sb-doped ZnO and Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin films.

To further understand the doping behaviour of Sb, XPS spectra of the Sb-doped p-type $Zn_{0.95}Mg_{0.05}O$ thin film were provided. Figure 4 shows the XPS spectra of Mg 1s and Sb $3d_{3/2}$ core levels of the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film. The concentrations of Sb and Mg in the film were calculated to be 2.5 at% and 5.4 at%, respectively, agreeing well with that in the targets. Figure 4(a) shows the Mg 1s narrow scan spectrum for the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film. The peak at 1303.7 eV is attributed to Mg–O bonding, which confirms that the Mg atoms in the deposited films are bonded to the O atoms. Figure 4(b) illustrates the Sb $3d_{3/2}$ narrow scan spectrum. The peak of the Sb $3d_{3/2}$ core level can be fitted into one Gaussian peak on deducting the base line, which indicates that only one chemical bonding state of Sb is existing in the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film. Isolated Sb may form Sb_{Zn} (Sb occupying Zn site), Sb_O (Sb occupying O site), or interstitial Sb_i. The Sb $3d_{3/2}$ peak centred at 540 eV is generally attributed to Sb–O bonding. Therefore, it is concluded that Sb incorporated in the film should exist as Sb_{Zn} rather than as Sb_O. However, isolated Sb_{Zn} acts as a donor rather than an acceptor, which will not result in p-type conductivity. Thus, it is reasonable to infer that another Sb-related acceptor state is existing in the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film. Recently, a model for large-size-mismatched group-V dopants in ZnO has been proposed [13], in which an Sb_{Zn}–$2V_{Zn}$ complex (Sb occupying Zn site and spontaneously inducing two Zn vacancies) has been reported to be the most likely defect to form a shallow acceptor level with low formation energy of 2.00 eV in Sb-doped ZnO. In addition, the direct observation of As on the Zn site has been reported in As-doped ZnO and a similar As_{Zn}–$2V_{Zn}$ complex has been proposed [14]. With these considerations, the clear p-type behaviour in the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film is most likely attributed to the Sb_{Zn}–$2V_{Zn}$ complex in the present case.

4. Conclusions

In summary, Sb-doped p-type $Zn_{0.95}Mg_{0.05}O$ thin films have been prepared by the PLD method. The incorporation of an Sb acceptor is confirmed by SIMS as well as by XPS.

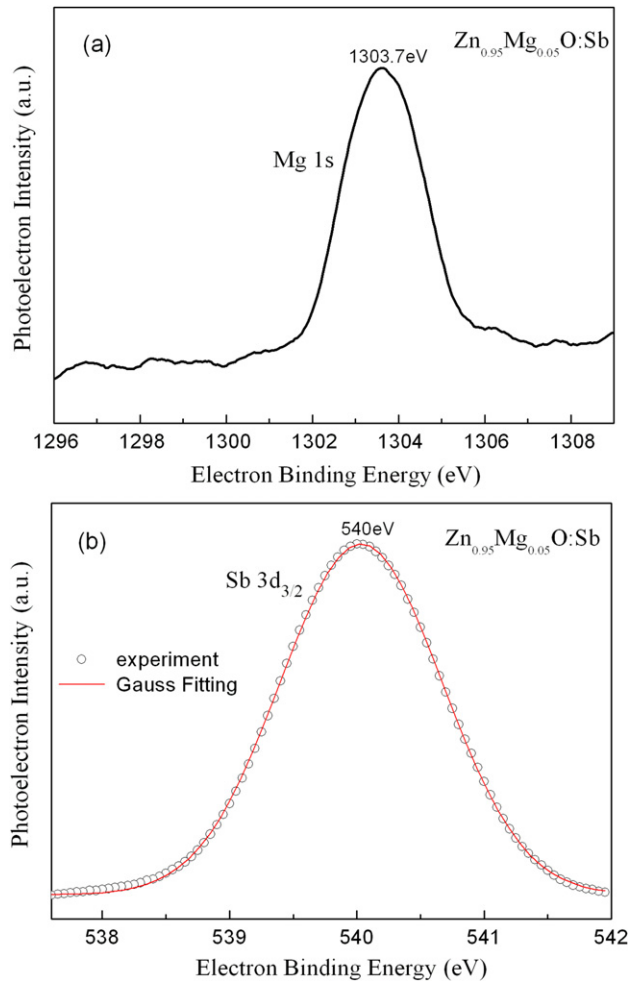**Figure 4.** XPS spectra of the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film grown at $400\,°C$: (a) Mg 1s, (b) Sb $3d_{3/2}$.

A blueshift in PL emission due to the introduction of Mg is observed in the $Zn_{0.95}Mg_{0.05}O$ thin film. The Sb_{Zn}–$2V_{Zn}$ complex is considered to be the most probable candidate to form a shallow acceptor level in the Sb-doped $Zn_{0.95}Mg_{0.05}O$ thin film. More detailed investigations on the Sb-doped ZnMgO thin films are in progress. These results will represent meaningful steps for ZnO/ZnMgO superlattices, quantum wells and UV optoelectronic devices.

Acknowledgments

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