

Characteristics of undoped and Sb-doped ZnO thin films prepared in different atmospheres by pulsed laser deposition

B. L. Zhu^{*,1}, S. J. Zhu¹, X. Z. Zhao², F. H. Su³, G. H. Li³, X. G. Wu³, and J. Wu¹

¹Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan 430081, People's Republic of China

²Department of Physics, Wuhan University, Wuhan 430072, People's Republic of China

³National Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, People's Republic of China

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* Corresponding author: e-mail zhubailin97@hotmail.com

Undoped and 0.56 at.% Sb-doped ZnO thin films were prepared by pulsed laser deposition (PLD) under vacuum and an oxygen pressure of 0.2 Pa with sintered ceramic as targets. The effects of Sb doping and deposition atmosphere on structure and optical–electrical properties of the films were studied by X-ray diffraction (XRD), scanning probe microscopy (SPM), Hall Effect measurement, transmittance spectra, and photoluminescence (PL) spectra. The results showed that undoped and Sb-doped films deposited under vacuum had better crystallinity, higher carrier concentration, lower bandgap (E_g), and single violet emission as compared with the films deposited in an oxygen pressure of 0.2 Pa. Compared with undoped ZnO film, Sb-doped ZnO film had higher carrier concentration and almost uniform E_g in both atmospheres, and it exhibited obviously improved crystallinity and green emission under an oxygen pressure of 0.2 Pa. The results implied that the deposition atmosphere strongly affected the growth kinetics of the films and intrinsic defect in the films, and Sb doping seemed also to affect the growth kinetics of the films under certain conditions and introduced Sb_{Zn} defects and possibly Sb_{Zn}-2V_{Zn} defects, thus the structure and optical–electrical properties of the films were modified by the deposition atmosphere and Sb doping.

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1 Introduction Due to a wide bandgap (E_g) of 3.37 eV and a large exciton binding energy of 60 meV, ZnO thin film has been widely applied to many areas such as transparent conductive window materials, light-emitting diodes (LED), laser diodes (LD), gas sensors, and ultraviolet detectors. The optical–electrical properties of ZnO thin films can be further modulated by using various dopants, such as group-IIA elements Mg, group-IIIA elements Al, group-IVB elements Zr, and group-VA elements Sb, etc. Among the doped elements, Sb can modify optical absorption, photoluminescence (PL), Raman spectra, n-type conductivity, gas sensing, and thermoelectric properties of ZnO bulk or thin films [1–6]. Recently, it was found that Sb doping into ZnO films can obtain p-type ZnO thin films [7–13].

Various techniques such as pulsed laser deposition (PLD) [8, 9, 14], molecular beam epitaxy (MBE) [10], metallorganic chemical vapor deposition (MOCVD) [11, 15,

16], RF magnetron sputtering [12, 17], and sol-gel [13, 18] had been used to prepare Sb-doped ZnO thin films. Among these techniques, PLD seems to be the most attractive since it can offer the potential of growing high-quality thin films at relatively lower substrate temperature than other techniques. Obviously, the properties of Sb-doped ZnO films are affected by process parameters such as deposition atmosphere, substrate temperature, and post-annealing treatment. Although Sb-doped ZnO films grown by PLD have been reported [8, 9, 14], the effects of process parameters of Sb-doped ZnO films have not been extensively investigated at present.

In this paper, we contrastingly study undoped and Sb-doped ZnO films deposited on glass substrates by PLD from pure ZnO and Sb-doped ZnO ceramic targets in different atmospheres. The aim is to evaluate the effects of



deposition atmosphere and Sb doping on the structure and optical-electrical properties of ZnO films.

2 Experimental procedure Undoped and Sb-doped ZnO thin films were deposited on glass substrates in a PLD system. The targets were high-purity ZnO and 0.56 at.% Sbdoped ZnO ceramic disks 2.5 cm in diameter and 0.4 cm in thickness. Glass sheets, which were used as the substrate for film deposition, were cleaned in an ultrasonic bath with acetone for 10 min before being loaded into the chamber. The substrates were placed parallel to the target surface with a distance of 5 cm. A pulsed excimer laser (KrF; $\lambda = 248$ nm, Lambda Physik, COMPex205) was used with an energy of 250 mJ/pulse, a pulse width of 25 ns and a repetition rate of 5 Hz. The laser beam was focused through a 50-cm focal lens onto a rotating target at a 45° angle of incidence. The substrate temperature was fixed at 350 °C, which was measured using a thermocouple and was controlled by a feedback-controlled heater. For all the films deposition, a deposition time of 20 min was maintained. The thin films were deposited under two different atmospheres: one was vacuum $(3 \times 10^{-3} \text{ Pa})$, and the other was introducing oxygen to maintain a pressure of 0.2 Pa after evacuating to 3×10^{-3} Pa.

An X-ray diffraction apparatus (XRD; Perking University, BDX3200) with Cu K α_1 incident radiation was used to identify the phase structure of the films. The surface morphology and roughness were investigated by a scanning probe microscope (SPM; Shimadzu, SPM-9500J3). The film thickness was measured by a nanostep instrument (Taylor Hobson, Form Talysurf S4C). The carrier concentration, mobility, and resistivity of the films were determined by the van der Pauw method at room temperature. The optical transmittance properties of the films were measured using a UV-visible-near-IR spectrometer (Varian, Cary 5000). The PL measurements of the films were performed using a He-Cd laser with an excitation wavelength of 325 nm.

3 Experimental results and discussion

3.1 Structural properties Figure 1 shows the XRD patterns of undoped and Sb-doped ZnO thin films deposited under vacuum and under an oxygen pressure of 0.2 Pa. Only a (002) diffraction peak is found in the patterns, indicating a strong *c*-axis orientation for all the films. The position and full width at half-maximum (FWHM) of (002) diffraction



Figure 1 (online color at: www.pss-a.com) XRD patterns of undoped and Sb-doped ZnO thin films deposited under vacuum and under an oxygen pressure of 0.2 Pa. Inset: The patterns are only shown within $32-36^{\circ}$, and the *y*-axis is on a logarithmic scale.

peak are listed in Table 1. As a whole, the deposition atmosphere has a remarkable effect on the XRD spectra of undoped or Sb-doped ZnO thin films. It is observed that the position of (002) diffraction peak $(2\theta_{(002)})$ of the films shifts to low angle when the atmosphere changes from vacuum to an oxygen pressure of 0.2 Pa. A strong (002) diffraction peak with narrow FWHM is observed under vacuum, but a weak (002) diffraction peak with broad FWHM is observed under an oxygen pressure of 0.2 Pa. Comparing the undoped and Sb-doped ZnO thin films deposited in the same atmosphere, the effects of Sb doping on the XRD patterns of thin films are also found. At both atmospheres, the $2\theta_{(002)}$ of Sb-doped ZnO thin films is lower than that of undoped ZnO thin films. Under vacuum, the intensity of the diffraction peak of Sbdoped ZnO thin films is lower and its FWHM of (002) diffraction peak is slightly larger than those of undoped ZnO thin films. But under an oxygen pressure of 0.2 Pa, the opposite results are observed. According to the Scherrer equation, the average crystallite size of the film can be estimated and is shown in Table 1. It is found that the films produced under vacuum have larger crystallite size than those films produced under an oxygen pressure of 0.2 Pa. Moreover, the films have almost the same crystallite size as those produced under vacuum, but the Sb-doped films have

Table 1 The position and FWHM of (002) diffraction peak, crystallite size from XRD, grain size from SPM, and the surface RMS roughness from SPM for the films deposited under vacuum and under an oxygen pressure of 0.2 Pa.

	undoped ZnO, vacuum	undoped ZnO, 0.2 Pa O ₂	Sb-doped ZnO, vacuum	Sb-doped ZnO, 0.2 Pa O ₂
20(000) (°)	33.9	33.75	33.84	33.62
FWHM (°)	0.686	1.644	0.703	1.056
crystallite size (XRD, nm) grain size (SPM, nm)	12.11	5.05 16.97	11.81 10.09	7.86 14.85
surface RMS roughness (nm)	_	0.887	0.741	1.22

larger crystallite size than undoped ZnO films produced under an oxygen pressure of 0.2 Pa.

The $2\theta_{(002)}$ of the films are lower than that of bulk ZnO (34.42°) , which implies that the lattice parameter c increases for the films. Furthermore, compressive stress is produced in the films due to the increase of c. Usually, the stress in the films includes the thermal stress and the intrinsic stress [19]. The thermal stress is caused by the difference in the coefficient of thermal expansion (CTE) of the substrate and the film. Due to the CTE of ZnO along the a-axis $(6.5\times 10^{-6}\,^\circ\text{C}^{-1})$ being smaller than that of glass (8– $10 \times 10^{-6} \,^{\circ}\text{C}^{-1}$), compressive stress should be produced in the films. Considering that the difference in CTE of ZnO film along the *a*-axis and glass substrate is not remarkable, and the growth temperature is low $(350 \,^\circ \text{C})$, the compressive stress in the films caused by the difference in CTE is negligible [19]. Moreover, the thermal stress in all films should be uniform due to the same growth temperature. However, compressive stress is obviously different in the films deposited in different atmospheres. So, it is thought that the intrinsic stress originating from defects in the films plays a very important role in the origin of the compressive stress in the films. The defects oxygen vacancies (V_O) and/or zinc interstitials (Zn_i) are formed easily when the films are prepared under vacuum and under an oxygen pressure of $0.2 \,\mathrm{Pa}$. The defects Zn_{i} cause c to increase and thus compressive stress is produced, but V_O results in opposite results. High compressive stress in the films indicates that Zn_i may be the predominant defects in the films. When the atmosphere changes from vacuum to an oxygen pressure of 0.2 Pa, the amount of V_O will further decrease due to the introduction of oxygen, and the amount of Zn_i correspondingly increases. Thus, stronger compressive stress is produced as the atmosphere changes from vacuum to an oxygen pressure of 0.2 Pa, and the $2\theta_{(002)}$ of the films shifts to a lower angle. For the doped ZnO films, the intrinsic stress originating from introduction of the dopant should also be considered. Generally, there are two possible positions, substitutional and interstitial, in the ZnO lattice where dopant ions can be introduced. The position of the introduced dopant ions depends on the ionic radius matching between the dopant and Zn^{2+} ion, as well as the radius of the interstice of the ZnO lattice. In this study, the radius of Sb^{3+} , Zn^{2+} , and octahedron interstice of ZnO are 0.092, 0.074, and 0.061 nm, respectively, thus it seems more reasonable that Sb^{3+} replaces Zn^{2+} [15]. The Sb³⁺ replacing Zn^{2+} results in an increase in c and thus compressive stress is further enhanced. This is consistent with the results that the $2\theta_{(002)}$ of Sb-doped films is lower than that of undoped ZnO films in both atmospheres.

The weakening of diffraction peak (*i.e.*, low intensity and large FWHM) implies that the crystallinity degrades with atmosphere from vacuum to an oxygen pressure of 0.2 Pa. In the reports about the effect of oxygen pressure on the structure of ZnO films by PLD, the researchers also observed this phenomenon [20, 21]. For example, Kim and Lee [20] found that the FWHM of the (002) diffraction peak Original

increased with oxygen pressure when ZnO films were deposited on Si(001) substrates by PLD under oxygen pressures of 0.07-66 Pa. When ZnO thin films were deposited on Al₂O₃ (001) substrates by PLD at oxygen pressures of 6.7-66 Pa, Jin et al. [21] also found that the FWHM of the (002) peak increased with oxygen pressure. As discussed by Kim et al., the possible reason for the deterioration in crystallinity for the film grown at the high oxygen pressure was due to the decrease of energy of deposition species. With the gas pressure increases, collisions of laser-ablated species with ambient gas increase, which results in the energy of deposition species arriving at the substrate decreasing to weaken the crystallinity of the films. The enhancement of the collisions also results in the amount of the species arriving at the substrate decreasing and thus the thickness of the film decreases. This is confirmed by the thickness measurement results that the films deposited under vacuum is about 130 nm but that deposited in an oxygen pressure of 0.2 Pa is about 80 nm. In addition, it is worth noting that the obvious deterioration in crystallinity under an oxygen pressure of 0.2 Pa, but good crystallinity is kept even at an oxygen pressure of 150 Pa in our previous report [22]. In Kim and Lee's [20] experiment, an obvious deterioration in crystallinity appeared at an oxygen pressure of 66 Pa. The crystallinity of the films is affected by the kinetics of atomic arrangements during deposition, and the kinetics is determined by the substrate temperature and the energy of the deposition species [20]. In addition to gas pressure during deposition, the energy of deposition species is also related to many other factors including laser energy, absorption coefficient and density of targets, and targetsubstrate distance. Compared with our previous report [22], lower laser energy in this study may causes degradation of the crystallinity even under an oxygen pressure of 0.2 Pa. For undoped and Sb-doped films deposited under vacuum, Sb doping into the ZnO lattice may cause the distortion of lattice, which results in the deterioration of the crystallinity of Sb-doped films. Under an oxygen pressure of 0.2 Pa, the energy of deposition species arriving at the substrate decreases; Sb atoms may increase the energy of the deposition flux and/or surface diffusion of Zn atoms, which improves the crystallinity of the films. Thus, the Sb-doped ZnO thin film has an improved crystallinity under an oxygen pressure of 0.2 Pa. This phenomenon has also been found in the Tb-, Mg-, and Sn-doped ZnO films by other researchers [23-25].

The typical SPM images of the films are shown in Fig. 2, and the grain size and surface root mean square (RMS) roughness obtained from the images are also shown in Table 1. It is seen from Table 1 that the grain size and surface RMS roughness of Sb-doped ZnO films increase when the atmosphere changes from vacuum to an oxygen pressure of 0.2 Pa. This result implies that the collisions of laser-ablated species with ambient atoms increase in number at high gas pressure to form larger particles and a coarse surface when arriving at the substrate. In the same atmosphere of oxygen pressure of 0.2 Pa, the grain size of Sb-doped ZnO films is





1.00x1.00µm



slightly lower, but its surface RMS roughness is obviously higher than those of undoped ZnO films.

500.00nm

3.2 Electrical properties Hall effect measurement indicates that all the films exhibit n-type conduction. The resistivity (ρ), carrier concentration (n), and mobility (μ) of the films are shown in Table 2. In the case of undoped or Sbdoped ZnO films, the carrier concentration of the film deposited under vacuum is higher than that of the films deposited in an oxygen pressure of 0.2 Pa. As mentioned above, Vo and/or Zni will be produced in an insufficient oxygen atmosphere, and Zni should contribute to the conductivity of ZnO films since the V_{O} is thought to be a deep donor in ZnO. When the deposition atmosphere changes from vacuum to an oxygen pressure of 0.2 Pa, the decrease of the amount of Zn_i results in the decrease of the carrier concentration. As for undoped films, the carrier mobility of the films deposited under vacuum is higher than that in an oxygen pressure of 0.2 Pa, but the opposite result is

observed for Sb-doped films. Normally, carrier mobility is related to impurity scattering and intercrystallite boundary scattering [23]. The V_O and/or Zn_i in undoped ZnO are provided as impurity scattering centers to hinder carrier motion. Intercrystallite boundary scattering is mainly controlled by crystallite size in the films. Obviously, the lower carrier mobility of undoped films deposited in an oxygen pressure of 0.2 Pa than that under vacuum can be attributed to its much smaller crystallite size. But for Sb-doped ZnO films, impurity scattering by defects in films may be dominant, thus the carrier mobility of the films deposited under vacuum is lower than that in an oxygen pressure of 0.2 Pa. The resistivity of the films is inversely proportional to the product of the carrier concentration and mobility, thus its change is controlled by the change of carrier concentration and mobility. As shown in Table 2, the resistivity of both undoped and Sb-doped films deposited under vacuum is lower than that in an oxygen pressure of 0.2 Pa.

Table 2 The resistivity (ρ), carrier concentration (n), and mobility (μ) of undoped and Sb-doped ZnO films deposited under vacuum and under an oxygen pressure of 0.2 Pa.

	undoped ZnO,	undoped ZnO,	Sb-doped ZnO,	Sb-doped ZnO,
	vacuum	0.2 Pa O ₂	vacuum	0.2 Pa O ₂
$\frac{n \text{ (cm}^{-3})}{\mu \text{ (cm}^2/\text{V s)}}$ $\rho (\Omega \text{ cm})$	$\begin{array}{c} 1.25 \times 10^{20} \\ 4.19 \\ 1.20 \times 10^{-2} \end{array}$	$\begin{array}{c} 4.16 \times 10^{19} \\ 3.46 \\ 4.34 \times 10^{-2} \end{array}$	$\begin{array}{c} 1.41 \times 10^{20} \\ 9.70 \\ 4.56 \times 10^{-3} \end{array}$	$\begin{array}{c} 9.94 \times 10^{19} \\ 10.16 \\ 6.18 \times 10^{-3} \end{array}$

In the same atmosphere of vacuum or oxygen pressure of 0.2 Pa, Sb-doped ZnO films have higher carrier concentrations than those of undoped ZnO films, which suggests that the Sb³⁺ ion occupies the site of the Zn²⁺ ion to supply the free electron. The carrier mobility of Sb-doped ZnO films is also higher than that of undoped ZnO films. Generally, the carrier mobility of doped films should be decreased due to introduction of the impurity. However, some defects caused by doping may provide the channels for electron transfer, and thus the carrier mobility increases [26]. Due to the increase of both carrier concentration and mobility for Sb-doped ZnO films, its resistivity is obviously lower than that of undoped ZnO films.

3.3 Optical properties The transmission spectra with wavelength from 280 to 2500 nm of undoped and Sbdoped ZnO films under vacuum and under an oxygen pressure of 0.2 Pa are shown in Fig. 3. Obviously, a steep absorption edge is observed at about 375 nm for all the films. About 80% transmittance is found from 375 to 2500 nm in the films deposited under an oxygen pressure of 0.2 Pa. The films deposited in the vacuum also have a gentle absorption edge from 375 to 500 nm, and the transmittance is about 80% above 500 nm. Usually, with increasing carrier concentration, the transmittance obviously decreases in the IR region due to the plasma resonance, which is frequently observed in transparent conducting oxide (TCO) films. However, the obvious decrease of transmittance in the IR region is not observed in this study. This is because the carrier concentration is not high enough $(4.16 \times 10^{19} - 1.41 \times 10^{20} \text{ cm}^{-3})$ to result in the appearance of plasma resonance. According to a related report, when the carrier concentration is higher than 3.4×10^{20} cm⁻³ the obvious decrease of transmittance in IR region can be observed [27]. It is seen from the inset of Fig. 3 that the absorption edge shifts to higher wavelength as the



Figure 3 (online color at: www.pss-a.com) Optical transmission spectra for undoped and Sb-doped ZnO films deposited under vacuum and under an oxygen pressure of 0.2 Pa. The inset shows the absorption edge region.



3.6

hυ (eV)

3.8

40

Figure 4 (online color at: www.pss-a.com) $(\alpha h \upsilon)^2$ as a function of the photon energy $(h \upsilon)$ for undoped and Sb-doped films deposited under vacuum and under an oxygen pressure of 0.2 Pa.

1.0x10¹²

8.0x10¹

6.0x10¹

2.0x10¹

0.0

3.0

32

 $(cm^{-2}eV^{2})$

) _z(ΩμΩ) 4.0x10¹

atmosphere changing from an oxygen pressure of 0.2 Pa to vacuum. In the same atmosphere, the positions of the absorption edges of undoped and Sb-doped ZnO films almost overlap.

The $E_{\rm g}$ can be obtained by extrapolating the linear portion of the $(\alpha h\nu)^2$ versus $h\nu$ curve to $(\alpha h\nu)^2 = 0$ in which α is the absorption coefficient and hv is the photon energy [22]. The plots of $(\alpha h \upsilon)^2$ versus photon energy $(h \upsilon)$ of the films deposited under different atmospheres are shown in Fig. 4. The obtained $E_{\rm g}$, shown in Table 3, indicates that the films deposited under vacuum have a lower E_g (3.35–3.36 eV) than the films deposited under an oxygen pressure of 0.2 Pa (3.39-3.40 eV), which is consistent with the position of the absorption edge. The shifts of the E_g as a function of oxygen pressure have been reported by some groups, but the results are rather confusing. For example, Wang et al. [28] observed that the $E_{\rm g}$ first increased with the oxygen pressure increasing from 10^{-5} to 1 Pa, then decreased with oxygen pressure further increasing to 30 Pa. Sun et al. [29] found that the E_{g} increased with oxygen pressure from 5 to 50 Pa. In our previous published paper, the E_{g} decreased with oxygen pressure increasing from 0.003 to 150 Pa [22]. In order to explain the shift of the E_{g} , different mechanisms have been suggested. For example, the increase of carrier concentration normally causes the increase of $E_{\rm g}$ due to the Burstein–Moss effect. This effect is due to the fact that the Fermi level moves into the conduction band or rises in the conduction band with

Table 3 The E_g from the transmission spectra for undoped and Sb-doped ZnO films deposited under vacuum and under an oxygen pressure of 0.2 Pa.

	undoped ZnO,	undoped ZnO,	Sb-doped ZnO,	Sb-doped ZnO,
	vacuum	0.2 Pa O ₂	vacuum	0.2 Pa O ₂
Eg	3.35	3.40	3.36	3.39

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increasing carrier concentration, and the filling of the conduction band by electrons will generally result in the valence electrons requiring extra energy to be excited by photons to higher-energy states in the conduction band. Hence, the optical bandgap increases with carrier concentration [30, 31]. However, the bandgap narrowing effect (bandgap renormalization) also occurs due to the effect of many-body carrier-ion interactions with increasing carrier concentration, which causes bandgaps to decrease with carrier concentration [30-32]. For example, Lu et al. [30] found that the E_g decreased with carrier concentration increasing from 5.4×10^{19} to 8.4×10^{19} cm⁻³ in Al-doped ZnO films. Other researchers observed that E_g began to decrease at higher carrier concentration (of the order of 10^{21} - 10^{22} cm⁻³) in Ga-doped ZnO and In₂O₃-ZnO films [31, 32]. In this study, as the deposition atmosphere changed from vacuum to an oxygen pressure of 0.2 Pa, the carrier concentration decreases for both undoped and Sb-doped ZnO films. However, the obtained E_{g} of the films deposited under an oxygen pressure of 0.2 Pa is larger than that deposited under vacuum. Therefore, the E_{g} shift is not governed by the Burstein-Moss shift. In addition to carrier concentration, the decrease of crystallite size is thought to increase the E_g due to the quantum size effect [33]; it is also found that the stress state in films affects the shift of the $E_{\rm g}$, *i.e.* $E_{\rm g}$ decreases for compressive stress but increases for tensile stress [34]. According to the XRD results, all the films are subject to the compressive stress, and the compressive stress in the films deposited in an oxygen pressure of 0.2 Pa is larger than that in the films deposited under vacuum, thus the $E_{\rm g}$ under an oxygen pressure of 0.2 Pa should be lower than that under vacuum. However, the E_g of the films under an oxygen pressure of 0.2 Pa is larger than that under vacuum. As discussed above, films deposited under an oxygen pressure of 0.2 Pa have much smaller crystallite size than the films deposited under vacuum, which may be the dominant factor to increase the E_g in the present study. Sb doping can cause the change of compressive stress, carrier concentration, and crystallite size of the films, but the E_{g} of the films is almost unalterable with Sb doping. This may be due to the fact that the effect of the above factors on the $E_{\rm g}$ just cancels each other out.

Figure 5 shows the room-temperature PL spectra obtained from the films deposited in different atmospheres. A broad violet emission at 3.03 eV is observed for undoped ZnO films deposited under vacuum. When the atmosphere changes to an oxygen pressure of 0.2 Pa, the undoped ZnO film has a weak UV emission at 3.25 eV and a broad violet emission at 3.10 eV. For the Sb-doped ZnO films, the film has a broad violet emission at 3.14 eV under vacuum, and it has a weak UV emission at 3.25 eV, a broad violet emission at 2.90 eV, and a green emission at 2.37 eV under an oxygen pressure of 0.2 Pa.

As reported in the literature, the typical PL spectra of ZnO films exhibit narrow UV emission and broad green emission peaks. The intensity of the UV emission peak is usually related to the crystallinity and stoichiometric ratio.



Figure 5 (online color at: www.pss-a.com) Room-temperature PL spectra of undoped and Sb-doped ZnO films deposited under vacuum and under an oxygen pressure of 0.2 Pa.

According to the XRD results, the crystallinity of the film deposited under vacuum is higher than that under an oxygen pressure of 0.2 Pa, but no UV emission is observed in the films deposited under vacuum. Although the film deposited under an oxygen pressure of 0.2 Pa has low crystallinity, its stoichiometric ratio improves due to the increase of oxygen. This implies that the UV emission is mainly governed by the stoichiometric ratio of the films in this study [35]. The energy of UV emission (3.22-3.25 eV) is lower than the E_g from the absorption edge (3.39-3.40 eV). This result had been also observed by other researchers, as due to the Stokes shift [36].

The violet emission from ZnO film has been reported in recent years, and different emission wavelengths and explanations were proposed. An emission located at about 395 nm (3.14 eV) is usually regarded as UV emission in most reports, and it is thought to originate from recombination of free excitons [37-39]. Recently, Cao et al. [40] observed a violet emission at 3.10 eV between the UV and green emissions, and attributed it to electron-hole recombination between the Zn_i shallow donor levels and the valence band. The violet emission at about 402 nm (3.08 eV) is not reported frequently, and it is assigned to the electron transition from the bottom of the conduction band to the zinc vacancy (V_{Zn}) level by Jeong et al. [41], and it is also thought to originate from the electron transition from conduction band tail states to valence band tail states by Wang et al. [42]. Violet emission at about 413 nm (3.00 eV) is observed frequently, and it is usually suggested to originate from electron transitions between the bottom of the conduction band and the V_{Zn} level [43]. The violet emission at about 420 nm (2.95 eV) is also observed frequently, and it is deduced to be the radiative transition between the defects level related to the interface traps existing at the intercrystallite boundaries and the valence band by Jin et al. [44, 45], and it is also thought to originate from the electron transition between the Zn_i level and the valence band [46]. According to the above discussion, ZnO films deposited under both atmospheres

have small crystallite size, which implies a large amount of intercrystallite boundary exists in the films. Thus, the observed violet emission is related to the defect level from the intercrystallite boundaries of the films. The defect level from intercrystallite boundaries varies with the crystallite size and carrier concentration. When ZnO films are prepared in insufficient oxygen atmosphere, the defect in ZnO films should be Zni and/or Vo, as mentioned above. Thus, in addition to the intercrystallite boundary defects, the violet emission of thin films maybe also related to the Zn_i defect, according to the previous reports. The Zn_i defects level has a 0.22 or 0.46 eV energy gap below the conduction band [40, 46]. For the Sb-doped ZnO films, substituted zinc (Sb_{Zn}) will produce a shallow donor level below the conduction band, which may also cause the violent emission. As a whole, the defects related to violet emission vary with preparation conditions, and finally they cause the changes of the violet emission perk position and the intensity of the films, but the exact mechanisms for different samples can not be concluded in this study. Further experimental and theoretical investigations are needed to address this issue.

As for green emission, it is also attributed to the electron transitions between different levels. For example, green emission was thought to be due to electron transition from V_{O} deep donor levels to the valence band for ZnO films deposited in insufficient oxygen [47]. But for ZnO films deposited in an oxygen-rich environment, observed strong green emission was ascribed to the electron transitions from the conduction band to the antisite oxygen (O_{Zn}) deep acceptor level [39]. The green emission is also attributed to the electron transition from V_O or Zn_i donor levels to the V_{Zn} acceptor levels [48]. As discussed above, the main defect is Zn_i in the films, thus the green emission cannot be attributed to V_O or O_{Zn} defect. In fact, if V_O or O_{Zn} defects are the main defects and thus cause the green emission in Sb-doped ZnO films deposited under an oxygen pressure of 0.2 Pa, the undoped ZnO films deposited in an oxygen pressure of 0.2 Pa should also show a green emission because of the same deposition condition. But no green emission is found in this sample. Noting that a number of Sb_{Zn}-2V_{Zn} complexes, as acceptors, may form under an improved oxygen pressure [7–9], the green emission in Sb-doped ZnO films deposited under an oxygen pressure of 0.2 Pa can be attributed to the electron transition from the Zn_i donor level to the $Sb_{Zn}-2V_{Zn}$ acceptor level.

4 Conclusions Undoped and Sb-doped ZnO thin films are prepared by PLD in different atmospheres. The results indicate that the structural and electrical–optical properties of the films are dependent on the deposition atmosphere and Sb doping. Compared with the films deposited under an oxygen pressure of 0.2 Pa, the films deposited under vacuum have higher crystallinity, larger crystallite size, higher carrier concentration, and a single violet emission. This is because the low oxygen pressure causes higher energy of deposition species and a low stoichiometric ratio of the films. In the same atmosphere, Sb-doped films have higher

compressive stress and carrier concentration than those of undoped ZnO films due to the formation of Sb_{Zn} defects and donor levels. Under an oxygen pressure of 0.2 Pa, Sb-doped ZnO films have improved crystallinity as compared with undoped ZnO, indicating that Sb doping seems to increase the energy of deposition species under certain conditions. The green emission appears in Sb-doped ZnO films when deposited under an oxygen pressure of 0.2 Pa, which might be attributed to the formation of Sb_{Zn}-2V_{Zn} acceptor levels. The optical spectra of the films may mainly depend on crystallite size, which results in similar E_g and optical transmittance at the same atmosphere and the higher E_g of the films deposited under an oxygen pressure of 0.2 Pa than that under vacuum.

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