Article ID: 1000-7032(2010)05-0613-06

Effects of Annealing Atmosphere and Temperature on the Structure and Photoluminescence of ZnO Films Prepared by Pulsed Laser Deposition

ZHANG Xia[1], LIU Yu-zhen[1*], KANG Chao-yang[2],
XU Peng-shou[2], WANG Jia-ou[3], KUI Re-xi[3]

(*1. Graduate University of Chinese Academy of Science, Beijing 100039, China;*
2. National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230026, China;
3. Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China)

Abstract Thin ZnO films were grown on silicon (111)/sapphire substrate via pulsed laser deposition technique and then some of the samples were treated with different rapid thermal annealing (RTA) conditions, such as annealing temperature ranging of 500 to 900 ℃ and annealing ambience (nitrogen and oxygen). Finally, these samples were characterized with X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), IR and photoluminescence (PL), respectively. It was observed that the quality and the grain size of thin ZnO films increased after annealing. Moreover, at the same lower annealing temperature, the films annealed under nitrogen ambience showed better qualities and few oxygen vacancies than those annealed under oxygen ambience. The experiment showed that the best annealing temperature under nitrogen ambience was 900 ℃ and the optimum annealing temperature under oxygen ambience was 800 ℃. Furthermore, as oxygen vacancies decreased, stronger green photoluminescence was detected, possibly related to the contents of the oxygen vacancies.

Key words: thin ZnO films; rapid thermal annealing; photoluminescence; XPS; oxygen vacancies
CLC number: O482.31 **PACS:** 78.55.Et **PACC:** 3220F; 7855E **Document code:** A

1 Introduction

ZnO is a wideband-gap (3.37 eV) compound semiconductor with a large exciton binding energy (60 meV), which has been considered as the most suitable material for UV devices when compared to the thermal energy (26 meV) of room temperature[1]. Moreover, its excellent optoelectronic properties and high chemical stability make it become one of the most promising materials for optoelectronic devices, including display devices, UV-light emitters, transparent power electronic devices, gas-sensing sensors, surface acoustic wave (SAW) devices and piezoelectric transdu-cers[2]. Due to the interesting applications, the PL properties of ZnO need to be studied thoroughly and numerous researchers have attempted to grow high crystalline ZnO films deposited on Si wafers. However, the larger lattice mismatch between ZnO and Si substrates has built up a challenge to finish it. Some researchers focused on the improvement of quality of the film by optimizing the growing conditions, such as deposition pressure, deposition time, substrate temperature[3] and growth ambient. On the other hand, the annealing treatment is an effective technique to improve crystallinity, which is usually adopted in the conventional furnace annealing. The alternative method is rapid thermal annealing. This technique facilitates the modeling of

Received date: 2009-10-19; **Revised date:** 2009-11-26
Foundation item: Projects supported by National Natural Science Foundation (50532070)
Biography: ZHANG Xia, born in 1985, female, Shandong Province. Her work focuses on photoluminescence and structure of thin films.
E-mail: zhangxia07@mails.gucas.ac.cn
*: Corresponding Author, E-mail: yzhenliu@yahoo.com, Tel: (010)88256071

the structure or the optical properties by controlling the heated temperature in seconds[4]. In order to investigate the structure and luminescence of ZnO, we prepared the films with PLD and post-annealed it under different temperatures and different ambiences. The results to the relationships between the structure and photoluminescence of the films and the annealing temperatures and ambiences are presented in this paper.

2 Experiments

Thin ZnO films were grown on silicon (111) / sapphire substrate by PLD technique. Pulsed KrF laser was operated at a wavelength of 248 nm and a repetition rate of 5 Hz. The laser energy density was 250 mJ/P. The target was a ceramic ZnO target (1-in diameter, 99.99% purity). A substrate holder was placed at 50 mm from the target. ZnO films were deposited at substrate temperatures of 500 ℃ for 30 min in the partial oxygen pressure of 0.13 Pa. Ten pieces of ZnO samples were cut from the as-deposited ZnO sample and was divided into two groups.

Then the ZnO samples were transferred to the RTP-500 rapid thermal predecessor and treated in the ranges of 500 ℃ to 900 ℃ for 60 s in oxygen and the other group in nitrogen (both with a purity of 99.99% and flux at 2 L/min) ambience, respectively. During the annealing process, the rising rate of the temperature was kept at 60 ℃/s.

All the samples were investigated by XRD system (Model MSAL-XD2, with Cu Kα of 1.540 6 nm and a power of 30 kV × 30 mA). To further study the effect of annealing ambience on the structure, selected samples were analyzed by IR and XPS. In addition, optical properties of the selected films were characterized by the PL measurements, which were carried out at room temperature using a He-Cd laser as a light source at an excitation wavelength of 325 nm.

3 Results and Discussion

3.1 Annealing Temperature

Fig. 1 and Fig. 2 shows XRD patterns of the as-deposited and RTA-treated thin ZnO films in the 2θ ranges of 30°~ 40° at different temperatures and different annealing ambience, respectively. As can be seen from XRD pattern, these films are all pure ZnO films with wurtzite-type structure showing (002) peak. The crystallite size of the samples can be calculated using the following Scherrer's equation: $D \approx 0.9\lambda/\beta\cos\theta$, where λ is the X-ray wavelength, θ, the diffraction angle and β, the value of full wave at half maxium (FWHM) in radians. The FWHM, diffraction angle and grain size are illustrated in Table 1. It can be noticed that there is a decrease of FWHM indicating the improvement of quality and a better (002) orientation through annealing in nitrogen ambience in temperature ranges of 500~ 900 ℃ and oxygen ambience in temperature ranges of 500~ 800 ℃. We believe that the improvement of crystallinity is due to the rearrangement of ZnO atoms in the film by the supply of sufficient thermal energy. Furthermore, the crystallinity of the films increases with the increasing post-annealing temperature. At relatively high temperature to some extent, atoms on surface have enough kinetic energy so that they can

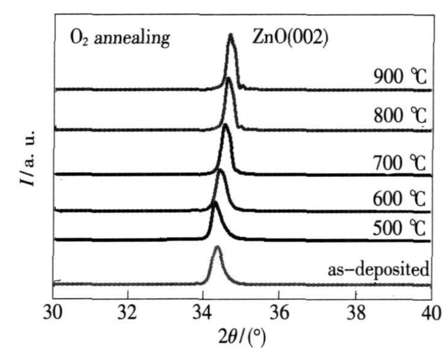

Fig. 1 XRD patterns of MgZnO films deposited in different temperature under 0.13 Pa

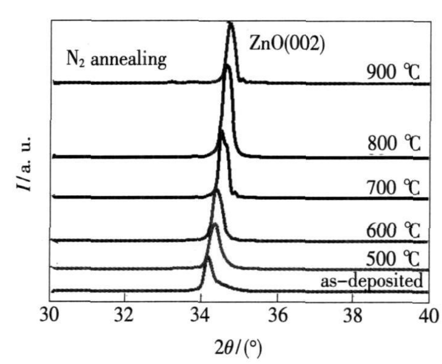

Fig. 2 XRD patterns of thin ZnO films as-deposited and annealed under nitrogen ambience

Table 1 The estimated parameters for the structure of ZnO/Si thin films at different annealing ambience and temperature

RTA temperature	N_2 ambience			O_2 ambience		
	FWHM /nm	Grain size/nm	2θ/(°)	FWHM /nm	Grain size/nm	2θ/(°)
As-deposited	34.261	0.318	25.84			
500 ℃	34.380	0.294	27.96	34.26	0.309	26.60
600 ℃	34.400	0.291	28.26	34.40	0.316	26.02
700 ℃	34.580	0.259	31.77	34.52	0.272	30.24
800 ℃	34.561	0.248	33.17	34.60	0.233	35.31
900 ℃	34.701	0.239	34.44	34.64	0.245	33.59

move quickly to lowest energy sites and have better quality. Moreover, at low temperatures, the film annealed at N_2 ambience displays better quality than that in O_2 ambience at the same temperature, which is consistent with the findings of Dae-Kue Hwang's groups[5]. Moreover, the films annealed under oxygen ambience show the best quality and the biggest grain size at 800 ℃, which indicates that 800 ℃ is the optimum annealing temperature for the film in this work, and this is consistent with M. Jung's research[6]. However, the crystal quality of thin ZnO/Si films might degenerate at annealing temperature 900 ℃ under oxygen ambience, which could be attributed to the discrepancy between ZnO and Si substrate during annealing, both the recrystallization and the interdiffusion between ZnO layer and Si substrate will be accelerated[4].

3.2 Annealing Ambience

To further investigate the effect of annealing ambience on the films, IR studies are carried out. Fig. 3 shows the IR spectra of the films annealed at 900 ℃ in oxygen and nitrogen ambience, respectively.

Fig. 3 shows that the as-deposited ZnO films contains three absorption bands at approximately 414, 614 and 1 108 cm^{-1}, which are typically ZnO absorption attributed to bending vibration absorption of Zn-O bond, local vibration of substitutional carbon in Si crystal lattice and vibration absorption of Si-O bond, respectively[7]. It can be noticed that the absorption peak of Zn-O becomes stronger after annealing and the FWHM becomes narrower, as clearly

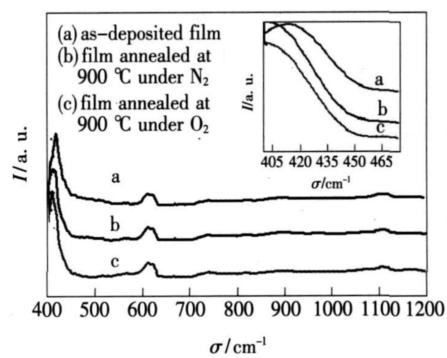

Fig. 3 IR spectra of as-deposited and annealed thin ZnO films. The inset shows the clear Zn-O absorption peak

seen in transmittance spectra, which concurs with XRD analysis. Moreover, ZnO absorption peak shows a red shift after annealing, indicating the decrease of vibration frequency ν. As $\nu \propto \sqrt{k/m}$, where k is the constant of Zn-O chemical bond and $m = \frac{m_{Zn} m_O}{m_{Zn} + m_O}$, we can conclude that the decrease of indicates less existence of Zn-O bond. This may be caused by the dissipation of oxygen from the films. No peaks related to nitrogen have been detected, indicating the nitrogen only plays as protecting gas. We surmise that the increase of grain size is accompanied with the dissipation of oxygen. Due to the oxygen ambience, the dissipation of oxygen is to some extent inhibited, the grain size is smaller than that annealed under nitrogen in the same temperature.

To further analyze the changes of oxygen during annealing under different conditions, the XPS analysis is performed to investigate the O1s core level binding energy. The binding energy was calibrated by taking carbon C1s peak (284.6 eV) as reference.

In Fig. 4, the O1s can be fitted by two peaks centered at (530±0.15) eV (O_1) and (531.9±0.15) eV (O_2). The O_1 is attributed to O^{2+} ion on the wurtzite structure of hexagonal Zn^{2+} ion array, surrounded by Zn atoms. The O_2 can be attributed to the presence of oxygen deficient regions within the matrix of ZnO. After annealing the ratio of O_2/O_1 decreased slightly, indicating a decrease in oxygen vacancies[8]. Likewise, the ratio increases a lot after annealing, indicating more oxygen vacancies producing during annealing under both ambience, which concurred with IR analysis. Furthermore, more oxygen vacancies exist in film annealed under oxygen than that annealed under nitrogen.

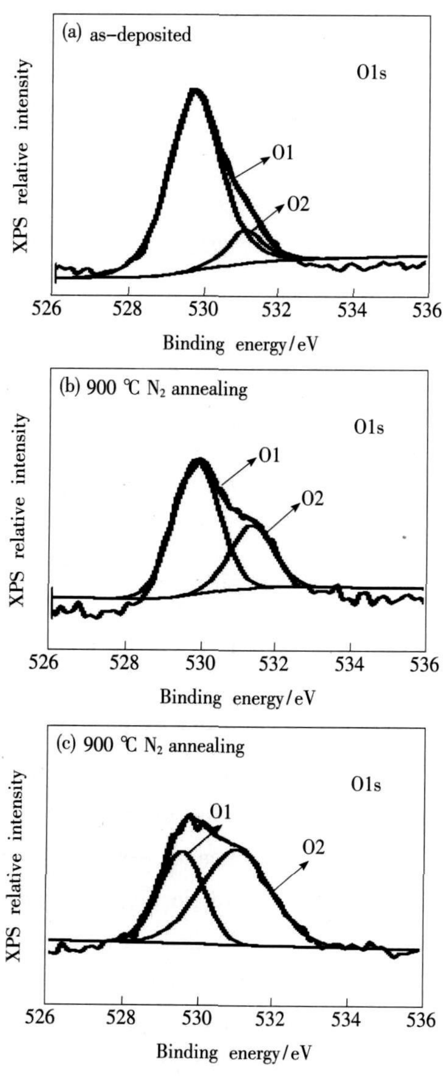

Fig. 4 O1s peak fitted with two peaks for as-deposited and annealed thin ZnO films

3.3 PL of ZnO Films Annealed at Different Ambience

As we know, the origin of the green photoluminescence of the ZnO films is always a controversy. Generally, the green emission is assumed to be caused by different intrinsic defects in ZnO film, such as oxygen vacancy, zinc vacancy and interstitial zinc[9~11]. As far as this question, spectra of the ZnO with different concentration of oxygen vacancies are presented in Fig. 5, which gives another evidence for the relationship between luminescence and oxygen vacancies. As seen from the Fig. 5, the film annealed under nitrogen ambience shows weak blue and green photoluminescence peaks located at 468 nm and 527 nm, respectively, while the film annealed under oxygen ambience has stronger peaks, which may result from the increasing oxygen vacancies. It could be concluded that the blue and green photoluminescence is related to oxygen vacancies[12,13].

Furthermore, the UV photoluminescence peaks is close to the quality of the film as the better-quality ZnO annealed under nitrogen shows stronger peak than that annealed under oxygen ambience.

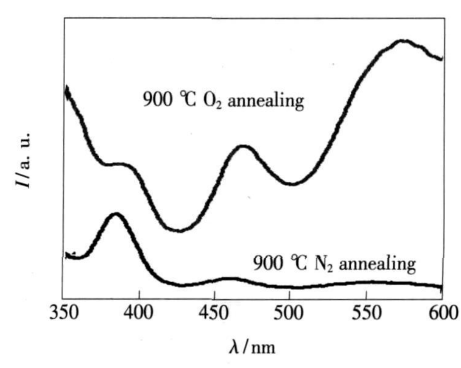

Fig. 5 PL spectra of thin ZnO films annealed at 900 ℃ under two oxygen and nitrogen ambience

4 Conclusion

In summary, highly c-axis-oriented thin ZnO films were grown on Si(111) wafers by PLD with post-thermal annealing under different ambience using RTP. RTP treatment not only improved the crystallinity of the film but also made the oxygen dissipate from the film, indicating more oxygen vacancies. Our experiment showed that the optimum temperature for annealing under oxygen ambience is 800 ℃ and the best annealing temperature under nitrogen ambience is 900 ℃ among the range of 500~900 ℃. In addition, more oxygen vacancies are formed in the films annealed under oxygen than that in nitrogen ambience at the annealing temperature 900 ℃. Furthermore, it is concluded that the green photoluminescence has close relationship with oxygen vacancies through our experiments. More experiments are underway to further investigate it.

References

[1] Ryu Y R, Zhu S, Budai J D, *et al*. Optical and structural properties of ZnO films deposited on GaAs by pulsed laser deposition [J]. *J. Appl. Phys.*, 2000, **88**(1): 201-204.

[2] Pearton S J, Norton D P, K Ip, *et al*. Recent progress in processing and properties of ZnO [J]. *Superlat. Microstruct.*, 2003, **50**(3): 293-340.

[3] Sun Bai, Zou Chongwen, Liu Zhongliang, *et al*. Microstructure and photoluminescence properties of ZnO thin films prepared by pulsed laser deposition [J]. *J. Vac. Sci. Technol.* (真空科学与技术学报), 2006, **26**(6): 446-450 (in Chinese).

[4] Hu S Y, Lee Y C, Lee J W, *et al*. The structural and optical properties of ZnO/Si thin films by RTA treatments [J]. *Appl. Surf. Sci.*, 2008, **254**: 1578-1582.

[5] Hwang Dae-Kue, Oh Min-Suk, Lim Jae-Hong, *et al*. ZnO-based light-emitting metal-insulator-semiconductor diodes [J]. *Appl. Phys. Lett.*, 2007, **91**(12): 121113-1-3.

[6] Jung M, Lee J, Park S, *et al*. Investigation of the annealing effects on the structural and optical properties of sputtered ZnO thin films [J]. *J. Cryst. Growth*, 2005, **283**(3-4): 384-389.

[7] Wei X Q, Zhang Z G, Liu M, *et al*. Annealing effect on the microstructure and photoluminescence of ZnO thin films [J]. *Mater. Chem. Phys.*, 2007, **101**(2-3): 285-290.

[8] Zhang P F, Liu X L, Wei H Y, *et al*. Rapid thermal annealing properties of ZnO films grown using methanol as oxidant [J]. *J. Phys. D: Appl. Phys.*, 2007, **40**(19): 6010-6013.

[9] Vanheusden K, Seager C H, Warren W L, *et al*. Mechanisms behind green photoluminescence in ZnO phosphor powders [J]. *Appl. Phys. Lett.*, 1996, **79**(10): 7983-7990.

[10] Bylander E G. Surface effects on the low-energy cathodoluminescence of zinc oxide [J]. *J. Appl. Phys.*, 1978, **49**(3): 1188-1195.

[11] Liu M, Kitai H, Mascher P, *et al*. Point defects and luminescence centres in zinc oxide and zinc oxide doped with manganese [J]. *J. Lumin.*, 1992, **54**(1): 35-42.

[12] Song Guoli, Sun Kaixia. Photoluminescence emission properties of nanocrystalline ZnO films [J]. *Acta Photonica Sinica* (光子学报), 2005, **34**(4): 590-593 (in Chinese).

[13] Zhang Xijian, Wang Guoqiang, Wang Qingpu, *et al*. Effect of annealing on optical properties of ZnO thin films [J]. *Chin. J. Lumin.* (发光学报), 2008, **29**(3): 451-454 (in Chinese).

退火温度及退火气氛对 ZnO薄膜的结构及发光性能的影响

张 侠[1], 刘渝珍[1*], 康朝阳[2], 徐彭寿[2], 王家鸥[3], 奎热西[3]

(1. 中国科学院 研究生院, 北京 100039; 2. 中国科学技术大学, 安徽 合肥 230026;
3. 中国科学院 高能物理研究所, 北京 100049)

摘要: 采用脉冲激光沉积技术在 Si/蓝宝石衬底上制备了 ZnO薄膜, 结合快速退火设备研究了不同退火温度

(500~900 ℃)及退火气氛(N_2, O_2)对薄膜的结构及其发光性能的影响。并优化条件得到具有最小半峰全宽及最大晶粒尺寸的薄膜。X射线衍射(XRD)结果表明:氮气氛下退火的 ZnO薄膜最佳退火温度为 900 ℃;氧气氛下退火的 ZnO薄膜最佳退火温度为 800 ℃。红外(IR)光谱中,退火后 Zn-O特征振动峰红移,说明在退火过程中,原子重新排布后占据较低能量位置;同样的退火温度下,氮气氛下退火的薄膜质量更优。同步辐射光电子能谱(synchrotron-based XPS)分别表征了未退火及 N_2, O_2下 900℃退火的 ZnO薄膜,分峰拟合结果表明氧气氛下退火产生更多的氧空位。结构表征结合光致发光(PL)谱表明绿光的发光峰与氧空位有关。

关 键 词: ZnO薄膜; 快速退火; 光致发光; X射线光电子能谱; 氧空位
中图分类号: O482.31 PACS: 78.55.Et PACC: 3220F; 7855E 文献标识码: A
文章编号: 1000-7032(2010)05-0613-06

收稿日期: 2009-10-19; 修订日期: 2009-11-26
基金项目: 国家自然科学基金(50532070)资助项目
作者简介: 张侠(1985-),女,山东人,主要从事薄膜材料的光学性质和微结构的研究。
E-mail: zhangxia071@mails.gucas.ac.cn
*: 通讯联系人; E-mail: yzhenliu@yahoo.com, Tel: (010)88256071