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Effect of Oxygen Pressure on the Optical Properties of MgZnO Films Prepared by PLD

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Abstract MgZnO films with highly *c*-axis orientation have been prepared on silicon (100) substrates via the excimer laser PLD method. The morphologies, structures, components, and optical properties have been systemically characterized by SEM, XRD, XPS, PL and absorption measurements. It has been found the oxygen pressure plays an important role in determining the structure and optical properties of the MgZnO film. The film grown at 1.5 Pa exhibits a unique nanocrystal structure with very high optical quality. It has been found that the UV emission peak is blue-shift about 86 meV with the oxygen pressure increasing from 5 to 45 Pa due to the increased solubility of Mg in MgZnO films. As for the green emissions located between 500~600 nm, they can be attributed to the deep-level emission of oxygen related defects. Our work will be of benefit to the further research to prepare epitaxial layer for growing ZnO nanoarrays by PLD technique.

Key words: MgZnO films; oxygen pressure; blue shift
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1 Introduction

ZnO is a wide band-gap semiconductor with important applications in surface acoustic wave (SAW) devices, gas sensors, piezoelectric device, transparent conductive film, and ultraviolet (UV) light-emitting diodes (LED). Energy band engineering is much demanded to further improve the photoelectrical performances of ZnO. By alloying with MgO (E_g ~ 7.7 eV), MgZnO has tunable band gap and can be used as barrier layer in quantum well, forming ZnO/(Mg, Zn)O hetero-junction or superlattice structures because of their closed lattice constants[1~6]. Various methods for MgZnO alloys preparation have been reported, such as pulsed-laser deposition (PLD), sol-gel, electrophoresis, metal organic chemical vapor deposition (MOCVD), and ultrasonic spray pyrolysis technique. Among these techniques, PLD has been widely used due to its unique merits such as stoichiometric deposition, high film quality, and excellent substrate flexibility. During PLD deposition, growth parameters such as substrate temperature, energy and frequency of pulsed laser, target to substrate distance, oxygen pressure, and deposition time must be carefully adjusted to obtain high quality film. To date, the effects of the growth conditions on the structures and optical properties of ZnO film have been carefully exploited[7~13]. However, relevant work for MgZnO film is rarely reported due to the implicit opinion that MgZnO film may have similar growth mechanism of ZnO.

Herein, we report the growth of MgZnO films at

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different oxygen pressure by PLD method. It has been found that the MgZnO films show very different structural and optical properties from that of ZnO films synthesized under the same conditions. In contrast to ZnO films, regular blue-shift of the UV emission peaks in PL spectra of MgZnO films has been observed while the oxygen pressure increases from 5 to 45 Pa. It is suggested the solubility of Mg in MgZnO film may increase with the increasing oxygen pressure, thus leading to the widening of the band gap.

Furthermore, we find that MgZnO film composed of hexagonal nanocrystals can be fabricated by adjusting the growth parameters. The nanocrystal film shows intense UV emission, which makes it an ideal candidate for high-performance ZnO-based photoelectronic devices.

2 Experiments

The mixed powder of ZnO (5N) and MgO (4N) with mole ratio of 9∶1 is ground, calcined, and sintered to form MgZnO target. The Si (100) substrates are ultrasonically cleaned in acetone and ethanol at room temperature for 10 min, respectively, and then dried by nitrogen gas flow before they are put into the deposition chamber. The substrates are placed parallel to the target at a distance of 48 mm. A pulsed excimer laser (KrF, λ = 248 nm, pulse duration 25 ns, COMPexPro102) is used and the frequency and power are adjusted to be 5 Hz and 160 mJ/pulse, respectively. The chamber is initially evacuated to 3×10^{-4} Pa, and then the oxygen is input and maintains at different pressure. Both the target and the substrate are rotated at a speed of 10 r·min^{-1} to ensure the uniform films. The deposition time for all the films is 30 min. A series of MgZnO films are deposited at a fixed substrate temperature of 650 ℃ and a varied oxygen pressure of 5, 15, 30, 45 Pa, respectively. As a comparison, ZnO films have been also prepared at the same deposition conditions. The structures and morphologies of MgZnO films have been investigated by X-ray diffraction (XRD, Cu Kα1 radiation, λ = 0.154 06 nm) and field-effect scanning electron microscopy (FESEM, Sirion 200), respectively. X-ray photoelectron spectroscopy (XPS) measurements are performed by a VG-MKII instrument with AlKα (1 486.66 eV) radiation. The optical properties of the films are characterized by steady-state/lifetime spectrofluorometer (FLUOROLOG-3-TAU). The absorption spectra of MgZnO films are measured by an UV-VIS-NIR spectrophotometer (DUV-3700).

3 Results and Discussion

Fig. 1 shows the XRD spectra of MgZnO films deposited by PLD with oxygen pressure ranging from 5 Pa to 45 Pa. It is worth noting that the ZnO (002) diffraction peak is the dominant peak in all the diffraction patterns, indicating the well *c*-axis growth orientation of the MgZnO films[14]. Fig. 2(a) depicts the relation of the lattice spacing *d* and the full width at half maximum (FWHM) of the (002) diffraction peak with the oxygen pressure. It is noted that the lattice spacing for the (002) plane of the MgZnO films is much smaller than the standard value of ZnO. The shrink of the MgZnO lattice is likely due to the smaller ion radius of Mg^{2+} (~0.057 nm) than that of Zn^{2+} (0.060 nm). These results indicate that Mg^{2+} substitutes successfully for Zn^{2+} into ZnO lattice. From Fig. 2(a), the FWHM of (002) diffraction peaks increase with the increasing of oxygen pressure, which is opposite to the result reported by Fan[12]. In order to evaluate the mean crystallite size of the films, we adopt the Scherrer formula $D=\frac{0.9\lambda}{B\cos\theta}$, where *D*, λ, θ, and *B* are the mean

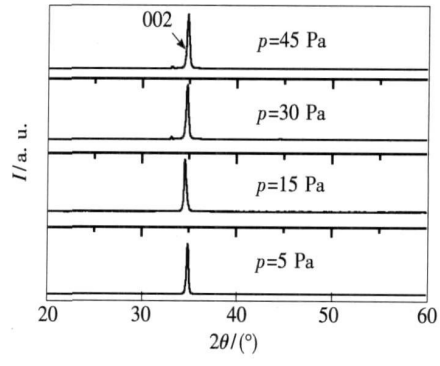

Fig. 1 XRD patterns of MgZnO films deposited at different oxygen pressure

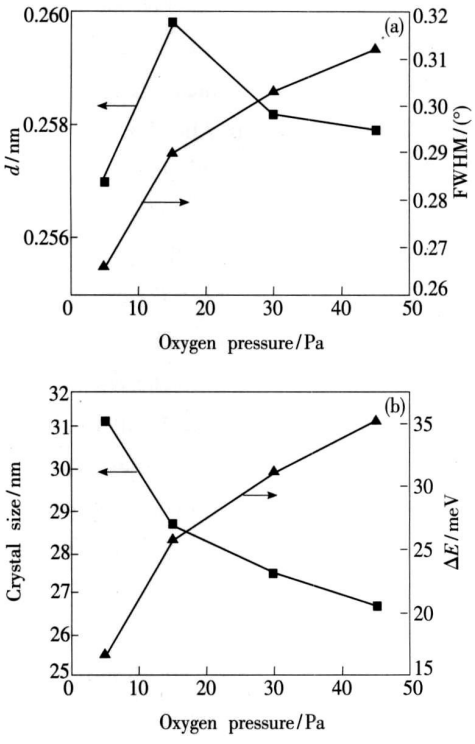

Fig 2　(a) The FWHM of (002) diffraction peaks and lattice spacing as the function of oxygen pressure; (b) The relationship of crystal size and widening of band-gap with the oxygen pressure

crystallite size, X-ray wavelength (0.154 06 nm), Bragg diffraction angle, and the FWHM of the diffraction peak of (002) around 34.66°, respectively. We obtain the mean crystallite sizes of 31.3, 28.7, 27.5, and 26.7 nm corresponding to the oxygen pressure of 5, 15, 30, and 45 Pa based on the above formula. According to quantum confinement theory, the band gap energy of a semiconductor depends on the crystallite size. For ZnO,

$$E_g(\mathrm{eV}) \approx E_{g0} + \frac{75.885}{d^2(\mathrm{nm}^2)} - \frac{1.902}{d(\mathrm{nm})},$$

$$\Delta E = E_g - E_{g0},$$

where E_g, d, E_{g0}, and ΔE are the band gap of the crystallite film, the crystallite size, band-gap of the bulk material, widened band gap, respectively[15]. Putting the crystallite size into above formula, we can get the relation of crystallite size with ΔE, as shown in Fig. 2(b). It is noticed that the widened band gap increases about 19 meV when the oxygen pressure increases from 5 to 45 Pa.

Fig. 3 shows the typical SEM images of the MgZnO films deposited at different experiment conditions. The thickness of the MgZnO film is measured to be ~ 270 nm from the cross-section view image of the film [inset in Fig. 3(d)]. Interestingly, the films deposited at 650 ℃ and 15 Pa possesses a very unique structure, *i.e.*, the film is mainly consisted of a large amount of hexagonal crystal grains with size in the range of 50~200 nm [Fig. 3(a, b)], in contrast to the relative smooth surface of the films deposited at other conditions [Fig. 3(c, d)]. Since MgZnO has the same wurtzite structure of ZnO, the hexagonal shape grains imply the well *c*-axis orientation of the film. These rod-like crystal grains grow vertical to the substrate and separated with each other. As we have known, most of the ZnO nanostructures such as nanorods and nanobelts have been synthesized by vapor-phase evaporation method with the aid of noble metals, and it remains a hard task to grow MgZnO nanostructures by PLD method. The primary results shown here demonstrate that PLD might be a potential method for high-quality MgZnO nanorods fabrication. As compared with previous reports, this method has advantages in many respects, such as low-cost, catalyst-free and high uniformity[7~10,13,14,16,17].

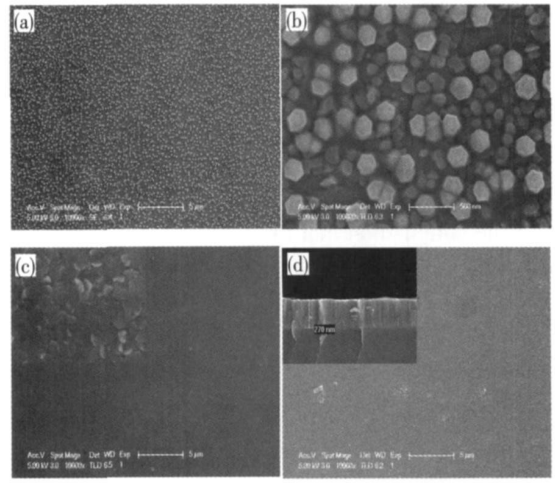

Fig 3　SEM images of MgZnO films deposited on silicon substrate by PLD method (a) grown at 650 ℃ and 15 Pa; (b) enlarged image of (a); (c) grown at 400 ℃ and 15 Pa, the inset is enlarged image; (d) grown at 650 ℃ and 30 Pa, the inset is the cross-section view image

Fig. 4 shows the XPS survey spectrum of the MgZnO film prepared by PLD at 650 ℃ with 15 Pa

oxygen pressure. The peaks in the spectrum can be indexed to be $Zn2p_{1/2}$, $Zn2p_{3/2}$, O1s, C1s, Zn3s, $Zn3p_{1/2}$, Zn3d, respectively. Moreover, the inset shows the enlarged core level XPS spectrum for the $Mg2p_{3/2}$ peak. From the spectrum, the atomic ratio of Mg: Zn: O is estimated to be 0.13: 1: 1.4 by using the corresponding sensitivity factors of $Mg2p_{3/2}$ 0.12, $Zn2p_{3/2}$ 4.8, and O1s 0.66. The large content of oxygen indicates that oxygen is rich in the MgZnO film. This result is different from that reported by Wei[18], in whose report the ratio of O to Zn is about 0.61 and oxygen is deficient.

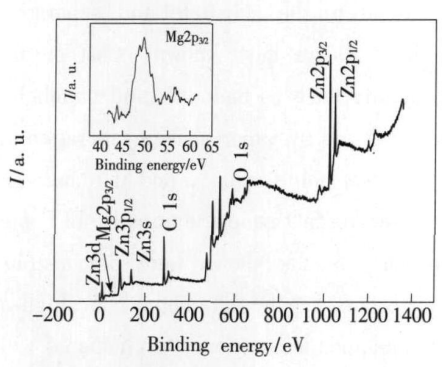

Fig. 4 XPS spectrum of MgZnO film prepared by PLD at 650 ℃ and 15 Pa

Fig. 5(a) depicts the room temperature PL spectra of MgZnO films deposited in different oxygen pressures at the same substrate temperature of 650 ℃. The UV emission peaks of the MgZnO are located at 356~365 nm, which is obviously shorter than that of pure ZnO (~375 nm) and is in agreement with the anticipation that the incorporation of Mg into ZnO should lead to the increase of band gap. Furthermore, it is found that the UV emission of the sample prepared at 15 Pa is much stronger than other samples, and on the contrary its visible emission is the weakest, which exhibits the highly optical properties of this sample. The intense emission of the 15 Pa sample can be attributed to its unique structure, *i.e.*, the film is composed of a large number of MgZnO nanorods, whereas the other samples have smooth surface. It is known the nanosizes of the nanorods can cause the confinement of the excitons and thus increase the probability of recombination, leading to the widening of band-edge emission. On the other hand, we note that the peak position of the UV emission strongly dependents on the oxygen pressure, which shifts toward shorter wavelength as the oxygen pressure increases from 5 Pa to 45 Pa [inset in Fig. 5(a)]. In contrast, the UV emission peaks of the ZnO films prepared at different oxygen pressure do not show obvious shift [Fig. 5(b)]. Our results prove that the effect of the growth conditions on the optical properties of MgZnO films are very different from that of ZnO films and thus highlight the importance of the systemic study on the films growth and properties of MgZnO. Our result is opposite to the previous report by Fan[12], who has observed that the UV peak is red-shifted at higher oxygen pressure. We ascribe this conflict to the difference of the change in growth method. In their experiment, pure Zn target instead of ZnO is used and the laser source is Nd-YAG laser, then ZnO film is formed via an oxidation process. Therefore, the crystal size of ZnO may increase with the increasing of oxygen pressure which results in the red-shift of the UV emission peak.

Besides the PL spectra, the shift of the UV peaks for the MgZnO films at different oxygen pressure is

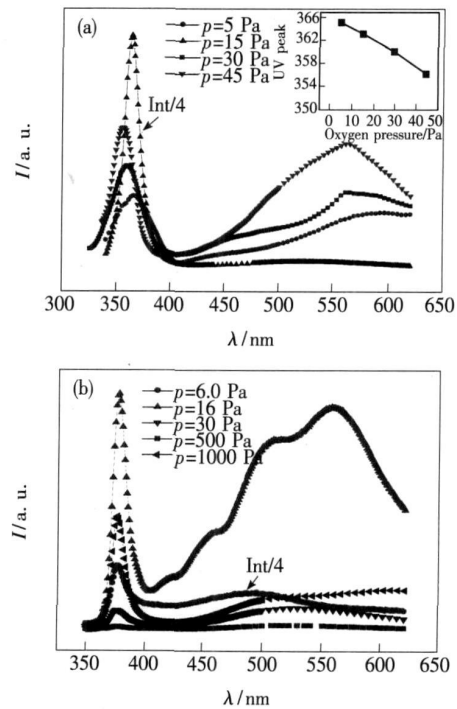

Fig. 5 PL spectra of MgZnO films (a) and ZnO films (b) deposited in different oxygen pressures at 650 ℃. The inset in (a) illustrates the relation of UV emission position with the oxygen pressure.

also confirmed by the absorption measurements, as shown in Fig. 6. From the α^2 vs photon energy curves it is seen the absorption edges obviously shift to the high energy direction while the oxygen pressure increases from 5 to 45 Pa. It is noticed that the result for 15 Pa sample has little deviation from the tendency. We contribute this deviation to the experiment inaccuracy and special samples. As we have known, films on quartz substrates are needed to perform the absorption measurements; the change in substrate may result in the small difference with the films on silicon substrates. Anyway, the approximate tendency of the blue-shift for the absorption edges still can be deduced from the absorption spectra. We note that the blue-shift of the UV emission is usually a result of the increased Mg content in MgZnO films, as that has been observed by Ohotmo[19] and Sharma[20].

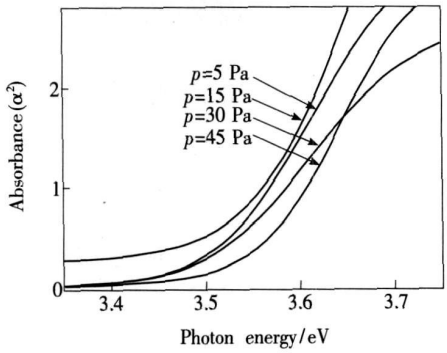

Fig. 6　Absorption coefficient α^2 of the MgZnO films deposited with different oxygen pressure vs photon energy

Although the underlying reason for the blue-shift of the UV emission in the optical measurements is not very clear, a possible mechanism is proposed to interpret this phenomenon based on the experiment results. The band-gap broadening caused by the quantum confinement effect might be responsible for the blue-shift since the crystal size in the MgZnO films increases with the increasing of oxygen pressure (Fig. 2b). However, the increase of the band gap is only about 19 meV as the pressure changes from 5 to 45 Pa. This value is far smaller than the 86 meV deduced from the PL spectra, indicating the change in the crystal size could not be the primary reason for the blue-shift observed in MgZnO films. On the other hand, we note that no visible blue-shift is observed for the ZnO sample prepared at the same conditions. The blue-shift occurs only in the MgZnO films. Therefore, it is reasonable to assume that Mg^{2+} in MgZnO film plays an important role in inducing the blue-shift of the UV emission. We suggest the solubility of the Mg atom may increase at higher oxygen pressure, and subsequently, leading to the broadening of the band gap. Indeed, opposite result of red-shift of the absorption edge for MgZnO films can be observed when the Mg content in MgZnO films has been reduced by annealing the films in oxygen atmosphere[21].

As for the visible emission of the MgZnO films between 500~600 nm, it is well known that there are five intrinsic defects in ZnO film including zinc vacancy V_{Zn}, oxygen vacancy V_O, interstitial zinc Zn_i, interstitial oxygen O_i, and antisite oxygen O_{Zn}[22]. During deposition, the concentration of the V_O and the Zn_i decrease with increasing oxygen pressure while the concentration of the V_{Zn}, O_i and O_{Zn} increase with increasing oxygen pressure[12]. The deep level (DL) emission peaks located at 594 nm (2.08 eV), 525 nm (2.36 eV), 565 nm (2.19 eV) and 562 nm (2.21 eV) in Fig. 5 (a) are corresponding to oxygen pressure of 5, 15, 30 Pa and 45 Pa, respectively. The energy levels of the intrinsic defects in ZnO films have been carefully calculated in previous works[11,12]. Accordingly, the DL peaks in our work can be assigned to the defect emission from O_i and O_{Zn}.

4　Conclusion

MgZnO films have been successfully prepared on silicon (100) substrates by the excimer laser PLD method. The influence of oxygen pressure on the structure and optical properties of the MgZnO has been studied. It has been found the film grown at 15 Pa and 650 ℃ exhibits a unique structure, *i.e.*, the film is composed of a large number of rod-like hexagonal grains, in contrast to the smooth films formed at other conditions. Moreover, the nanocrystal film has a high optical quality with a strong UV emission and a weak visible emission. The UV peak shifts from 3.397 to 3.483 eV for the MgZnO as the oxygen pressure increases from 5 to 45 Pa, whereas no

visible shift can be observed in ZnO films prepared at the same conditions. The blue-shift of the UV peaks is attributed to the increased solubility of Mg in MgZnO films at higher oxygen pressure. This phenomenon is also confirmed by the absorption measurements, in which the similar tendency of absorption edges has been observed. As to the green emissions of MgZnO located between 500~600 nm, they can be assigned to be the defect emission from O_i and O_{Zn} at an oxygen rich growth condition.

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氧气压强对 PLD 制备 MgZnO 薄膜光学性质的影响

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摘要: 使用准分子脉冲激光沉积(PLD)方法在 Si(100)基片上制备了高度 *c* 轴取向的 MgZnO 薄膜。分别使用 SEM、XRD、XPS、PL 谱和吸收谱表征了薄膜的形貌、结构、成分和光学性质。实验发现氧气压强对 MgZnO 薄膜的结构和光学性质有重要影响。当氧气压强由 5 Pa 增大到 45 Pa 时, 薄膜的 PL 谱紫外峰蓝移了 86 meV, 表明氧气压强的增大提高了 MgZnO 薄膜中 Mg 的溶解度。在 15 Pa 氧气压强下制备的薄膜显示了独特、均匀的六角纳米柱状结构, 其 PL 谱展示了优异的发光特性, 具有比其他制备条件下超强的紫外发射和微弱的可见发光。500~600 nm 范围内的绿光发射, 我们讨论其机理可能源于深能级中与氧相关的缺陷。使用 PLD 得到纳米柱状结构表明: 优化制备条件, 可望使用 PLD 制备 ZnO 纳米阵列的外延衬底; 可使用 PLD 技术开发基于 ZnO 纳米结构的高效发光器件。

关　键　词: MgZnO 薄膜; 氧气压强; 蓝移
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