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Annealing Effect on Smoothness and Composition of Cubic-phase $Mg_{0.57}Zn_{0.43}O$ Thin Film

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Abstract: Annealing behavior for cubic-phase $Mg_{0.57}Zn_{0.43}O$ thin films grown at 450 ℃ by metal-organic chemical vapor deposition were studied. After annealed at 550, 650, 750 and 850 ℃ in oxygen atmospheres, the crystal quality and surface smoothness of the thin films were improved significantly. Their bandgap shifts continuously to the higher energy the increasing annealing temperature. Confirmed by energy dispersive X-ray spectra, the enlarged bandgap was caused by the decrease of Zn content during annealing. Phase separation of the $Mg_{0.57}Zn_{0.43}O$ films with significant surface roughening can also be observed during annealing at 950 ℃.

Key words: MgZnO alloy; thermal annealing; surface morphology; grain size

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1 Introduction

With the increasing interest in ultraviolet photon detectors, wide bandgap semiconductors materials attract more and more attention[1-5]. MgZnO is a good candidate for UV detection due to its large tunable bandgap covers solar blind band along with ZnO and MgO wafers are developed[6]. However, phase separation may still be an obstacle for fabricating high quality thin film. A few solar blind photon detectors based on single phase MgZnO films were reported[7-8], but their performance in dark current and sensitivity still can not comparable with AlGaN-based ones. Some groups had reported that the quality and surface smoothness can be greatly improved by thermal annealing[10-11]. However, it should be noticed that thermal annealing indeed plays an accelerator for phase separation in MgZnO[12].

In this letter, cubic-phase $Mg_{0.57}Zn_{0.43}O$ thin films were grown by low pressure metal-organic chemical vapor deposition (LP-MOCVD). The evolvements of structure and optical properties during annealing in O_2 atmosphere from 550 to 950 ℃ were studied. Successfully, the improved crystal quality and surface smoothness had been obtained.

2 Experiments

MgZnO thin films were grown on *c*-plain sapphire substrate by LP-MOCVD. Dimethyl dicyclopentadienyl magnesium, diethyl zinc and high pure oxygen were employed as the precursors, and nitrogen as carrier gas. The deposition temperature was 450 ℃, the thickness of MgZnO film was about 300 nm.

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The as-grown MgZnO films were annealed in O_2 for 30 min at 550, 650, 750, 850, 950 ℃, respectively. The composition of the as-grown and the annealed MgZnO thin films was measured by energy dispersive X-ray spectroscopy (EDS). The morphology was characterized using a HITACHI S-4800 scanning electron microscope (SEM). The crystal structure was evaluated by X-ray diffraction (XRD) with Cu Kα (0.154 nm) line source. The absorption spectra were recorded using a Shimadzu UV-3101PC scanning spectrophotometer.

3 Results and Discussion

Fig. 1 (a) ~ (f) showed the SEM images of the as-grown and annealed MgZnO thin films. With the increasing annealing temperature, the grain on the surface was fused with each other and the surface get smoother gradually. After annealing at 650 ℃, the sample begins to show a compact surface. For the case of 750 ℃, the surface get even smoother, although a few grains are remained. At 850 ℃, as shown in Fig. 1(g), the sample shows a complete smooth surface and the regular triangle veins corresponding to the atom arrangement in the (111) plane of cubic lattice. As we know, high surface energy will be released by smoothening accompanied with atom migration at high temperature. Therefore, thermal annealing is considered as an efficient way to improve the surface smoothness. But, too high temperature also brings phase separation of metastable alloys. At 950 ℃, the surface smoothness degrades abruptly. Large grain was observed on the sample surface, which assigned to phase separation. XRD were performed to analyze the structure evdement. For all the samples, the θ-2θ scanning showedsimilar diffraction curve, so only one typical pattern was shown in Fig. 2. All the samples are crystallized in single cubic phase with (111) orientation. The inset showed the full width at half maximum (FWHM) of the MgZnO (111) peak as a function of annealing temperature. When the temperature increase to 850 ℃, the FWHM of (111) peak narrowed from 0.23° to 0.13°, corresponding to grain size varing from 38 nm to 67 nm, which calculated by Scherrer formula. The growing-up of grains supports the surface morphology evolvement depicted by SEM images. When the temperature increased to 950 ℃, no new peaks are observed in the XRD patterns, except the peak from(111) peak showed.

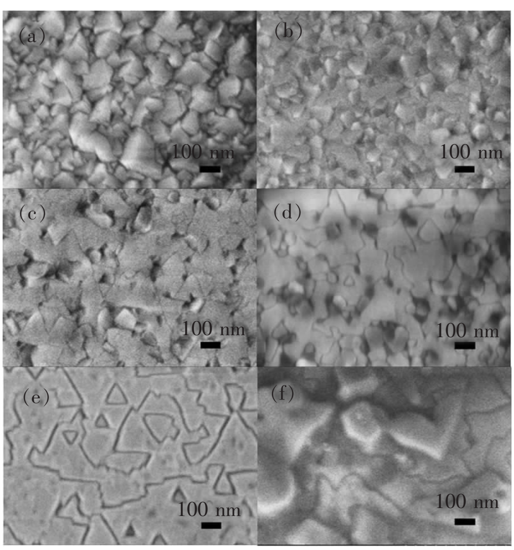

Fig. 1 SEM images of (a) the as-grown and the samples annealed at (b) 550 ℃, (c) 650 ℃, (d) 750 ℃, (e) 850 ℃ and (f) 950 ℃.

Comparing with XRD, absorption spectroscopy is a more sensitive tool for characterizing species with minute mounts[13]. Absorption spectra of the MgZnO thin films were shown in Fig. 3. For the samples annealed at 550 ~ 850 ℃, the absorption edge shifts to higher energy gradually with the increasing temperature. Due to the difference of vapor pressure, more Zn atoms than Mg escape from the sample at higher temperature, which brings more Mg content and then the blue shift of absorption edge. After annealed at 950 ℃, a new absorption edge appears at about 360 nm with the continuous blue shift. It indicates that the cubic MgZnO separates

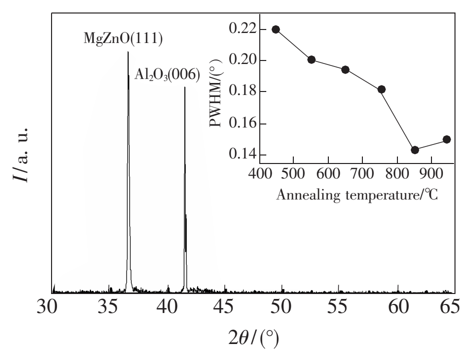

Fig. 2 Logarithmic scaled XRD patterns of the samples. inset: the FWHM of MgZnO (111) diffraction peak annealed at 550, 650, 750, 850 and 950 ℃.

into two phases with different bandgap. The new generated phase possesses such a low Mg content that the absorption edge is close to the pure ZnO[14]. It distributes in the old phase randomly, resulting in the Mg content fluctuation of the sample, and then the lattice constant fluctuation. That accounts for the showed widening of the (111) peak in XRD.

Fig. 4 showed a typical EDS spectrum of the MgZnO, where no signal from impurities were observed except Al from substrate. The inset is the Zn content evolvement in MgZnO thin films VS annealing temperature. That the Zn content decreases from 0.43 to 0.36 supports the blue shift of the absorption edge.

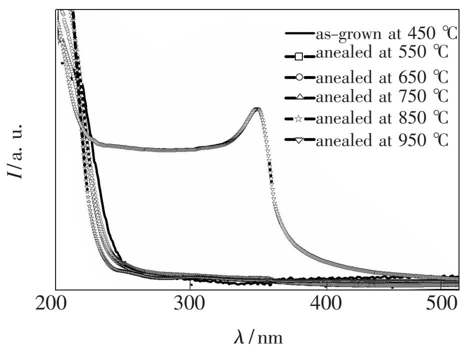

Fig. 3 Absorption spectra of the as-grown MgZnO and the samples annealed at 550, 650, 750, 850 and 950 ℃.

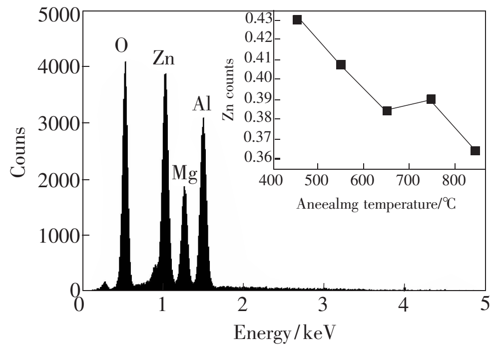

Fig. 4 EDS spectrum of the as-grown MgZnO and the samples annealed at 550,650,750,850 ℃. The inset shows Zn content as a function of annealing temperature.

4 Conclusion

The annealing evolution of cubic $Mg_{0.57}Zn_{0.43}O$ thin film that grown by MOCVD was studied. It was found that the surface smoothness and crystal quality were improved significantly with the increasing annealing temperature from 550 to 850 ℃. Simultaneously, the Zn content showed a continuous decrease from 0.43 to 0.36, which is attributed to the vapor pressure difference between Zn and Mg atoms. The phase separation occurs at 950 ℃. In summary, thermal annealing is an effective way to improve the quality of MgZnO alloys thin films.

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热处理对立方相结构 $Mg_{0.57}Zn_{0.43}O$ 合金薄膜表面和组成的影响

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摘要: MgZnO 合金具有可覆盖日盲紫外波段的禁带宽度和晶格匹配的单晶衬底,是理想的日盲紫外探测材料。由于 MgO 和 ZnO 分属立方相和六角相,分相问题使高质量单一相 MgZnO 难以获得。热处理是提高薄膜结晶质量的有效手段。利用 MOCVD 方法制备了单一立方相 $Mg_{0.57}Zn_{0.43}O$ 合金薄膜,研究了薄膜的退火行为对薄膜结构和光学性能的影响。研究发现,450 ℃的原生样品经过 550,650,750,850 ℃氧气氛退火后,薄膜的结晶特性和表面形貌得到明显的改善。随着退火温度的增加,薄膜吸收截止边逐渐蓝移,带隙展宽。X 光电子能谱分析发现,随着退火温度增加,Zn 含量逐渐减小,这种现象被归结为组分蒸汽压的差异。在退火温度达到 950 ℃时,样品发生了分相,出现了低 Mg 含量的六角相 MgZnO。

关 键 词: MgZnO 合金; 热退火; 表面形貌; 晶粒尺寸

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