# Effects of Mg doping content and annealing temperature on the structural properties of $Zn_{1-x}Mg_xO$ thin films prepared by radio-frequency magnetron sputtering*

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The doping content of Mg plays an important role in the crystalline structure and morphology properties of $Zn_{1-x}Mg_xO$ thin films. Here, using radio-frequency magnetron sputtering method, we prepared $Zn_{1-x}Mg_xO$ thin films on single crystalline Si(100) substrates with a series of $x$ values. By means of X-ray diffraction (XRD) and scanning electron microscope (SEM), the crystalline structure and morphology of $Zn_{1-x}Mg_xO$ thin films with different $x$ values are investigated. The crystalline structure of $Zn_{1-x}Mg_xO$ thin film is single phase with $x<0.3$, while there is phase separation phenomenon with $x>0.3$, and hexagonal and cubic structures will coexist in $Zn_{1-x}Mg_xO$ thin films with higher $x$ values. Especially with lower $x$ values, a shoulder peak of 35.1° appearing in the XRD pattern indicates a double-crystalline structure of $Zn_{1-x}Mg_xO$ thin film. The crystalline quality has been improved and the inner stress has been released, after the $Zn_{1-x}Mg_xO$ thin films were annealed at 600 °C in vacuum condition.

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In recent years, ZnO has received a lot of interest as a promising candidate for ultraviolet optical applications, such as light-emitting diodes, laser diodes and ultraviolet photodetectors due to its wide bandgap of 3.37 eV and large exciton binding energy of 60 meV[1-12]. In order to design ZnO-based devices, it is important to modulate the bandgap of ZnO. The bandgap of Mg-doped ZnO may be adjusted from 3.37 eV (pure ZnO) to 7.8 eV (pure MgO). Moreover, the substitution of Zn with Mg cannot induce significant change in the lattice constant, as the ionic radius of Zn is close to that of Mg. This is essential for bandgap engineering as well as homogeneous or heterogeneous p-n junction device design. The growth method and parameters have large influence on the crystalline structure of $Zn_{1-x}Mg_xO$ thin films. Cong et al[1,2] reported the effect of growth ambient on the structure and properties of $Zn_{1-x}Mg_xO$ thin films using radio-frequency sputtering, and they found that Mg concentration, structure and bandgap of the $Zn_{1-x}Mg_xO$ film can be tuned by increasing the $N_2$ partial pressure ratio in the $Ar+N_2$ ambient, but cannot be tailored by changing the $N_2$ partial pressure ratio in the $N_2+O_2$ ambient. Fan et al[6] reported a high performance solar-blind ultraviolet photodetector based on mixed-phase $Zn_{1-x}Mg_xO$ thin film, and the mixed phase of $Zn_{1-x}Mg_xO$ was the key to the development of ultraviolet photodetectors. The phase separation phenomenon appearing with $x$ larger than 0.25 was also reported for $Zn_{1-x}Mg_xO$ thin film prepared from sol-gel method[13,14].

In this paper, the $Zn_{1-x}Mg_xO$ thin films were grown by radio-frequency magnetron sputtering with different $x$ values. The effects of Mg doping content and annealing temperature on the structure and morphology of the $Zn_{1-x}Mg_xO$ thin films are discussed. The crystalline structure of $Zn_{1-x}Mg_xO$ thin film is single phase with $x<0.3$, while there is phase separation phenomenon of hexagonal and cubic structures with $x>0.3$. The crystalline quality and inner stress of $Zn_{1-x}Mg_xO$ thin film are improved and released by vacuum annealing process at 600 °C.

The Mg doped ZnO ceramic targets with different Mg contents were prepared by the following method: first, ZnO (99.99%) and MgO (99.99%) fine powders were mixed and grinded, preheated and pressed into target shape with dimension of $\Phi$60 mm×5 mm by 0.5 MPa oil pressure machine, then the target was sent into a muff

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furnace and sintered at 1 050 °C for 8 h, finally cooled to the room temperature. Six $Zn_{1-x}Mg_xO$ targets with Mg contents of 15%, 25%, 35%, 40%, 50% and 60% were prepared by the above method, and named as $Zn_{0.85}Mg_{0.15}O$, $Zn_{0.75}Mg_{0.25}O$, $Zn_{0.65}Mg_{0.35}O$, $Zn_{0.6}Mg_{0.4}O$, $Zn_{0.5}Mg_{0.5}O$ and $Zn_{0.4}Mg_{0.6}O$, respectively.

The $Zn_{1-x}Mg_xO$ thin films were prepared using radio-frequency magnetron sputtering. Step 1, the single crystalline Si(100) substrates were cut into pieces with dimension of 10 mm×10 mm and ultrasonic cleaned in acetone and de-ionized (DI) water, then sent into the vacuum chamber after being dried with $N_2$ gas. Step 2, the ZnO buffer layer was deposited on Si(100) substrate, the temperature was kept at 450 °C, the deposition time was 15 min, and the thickness of the ZnO buffer layer is about 50 nm. Step 3, the $Zn_{1-x}Mg_xO$ thin film was deposited on ZnO/Si(100) with the same substrate temperature, the deposition time was 50 min, and the thickness of this layer was about 150 nm. The working Ar (99.999%) pressure was 2.5 Pa, the radio frequency power was 100 W, and base vacuum pressure was $1\times10^{-4}$ Pa. During the deposition, different $O_2$ partial pressures and annealing times were selected to investigate structural and luminescent variations of the thin films.

The crystalline structure of $Zn_{1-x}Mg_xO$ thin film was determined by X-ray diffraction (XRD) using Rigaku diffraction meter with Cu $K_{\alpha1}$ radiation ($\lambda$=0.154 05 nm), and the scanning rate is 8°/min. The scanning electron microscope (SEM, ZEISS, SIGMA) was used to characterize the crystalline size and morphology of the annealed samples. All the measurements were performed at room temperature.

In order to investigate the influence of Mg content on the $Zn_{1-x}Mg_xO$ thin film, we prepared four samples with Mg doping contents ranging from 15% to 50%, and all of these four samples were annealed at 350 °C for 1 h. Fig.1 displays the structure information of these four samples from XRD measurement.

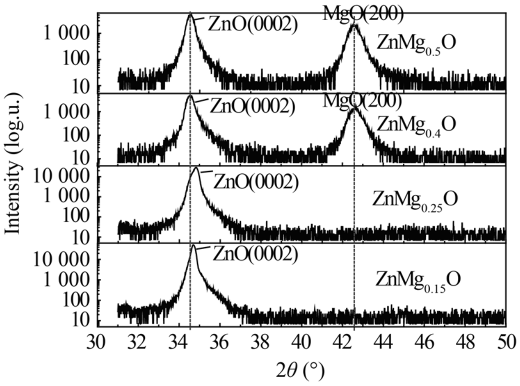



**Fig.1 XRD patterns of $Zn_{1-x}Mg_xO$ thin films with $x$=0.15, 0.25, 0.4, 0.5**

XRD results reveal that the films display different structures with different $x$ values: for $x<0.3$, the film is hexagonal ZnO structure, and there exists only one diffraction peak of (0002), namely single crystalline; for $x>0.3$, there are two different structures, one is hexagonal ZnO, while the other is cubic MgO, which means there exists phase separation for higher $x$ values. Besides, it should be noticed that there is a shoulder peak for ZnO (0002), which will be shown in detail in Fig.2.

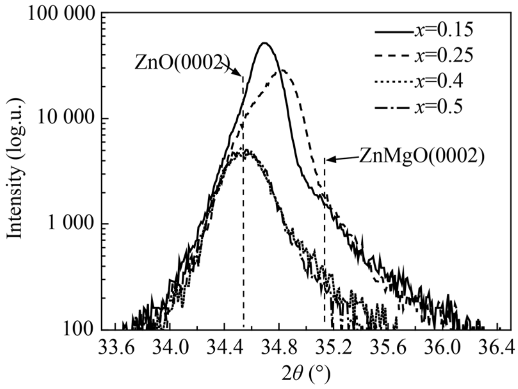



**Fig.2 Detailed information of (0002) peak for $Zn_{1-x}Mg_xO$ thin films with $x$=0.15, 0.25, 0.4, 0.5**

In the XRD diagram of (0002) peak for $Zn_{1-x}Mg_xO$ thin films with $x$=0.15, 0.25, 0.4, 0.5, it can be observed that for Mg concentration with higher $x$ values of 0.4 and 0.5, there is only one main (0002) ZnO peak at 34.5°, while with lower $x$ values of 0.15 and 0.25, a new peak appears with diffraction angle of 35.1° besides 34.5°. So we believe that as for $Zn_{1-x}Mg_xO$, the real (0002) peak position is at 35.1°. The peak height in lower $x$ case is much larger than that in higher $x$ case for $Zn_{1-x}Mg_xO$ thin films, which indicates that the crystalline quality is better for the lower $x$ values, as Mg concentration increases, the crystalline quality becomes worse.

Although the growth temperature is 450 °C, usually annealing is an important step to influence the crystalline quality. So we choose two $x$ values of 0.35 and 0.65, and two annealing temperatures of 350 °C and 600 °C at vacuum. From Fig.3 we can see that there is a shift of peak position for $x$=0.65, while there is no change for $x$=0.35 (not shown), and the (0002) peak position moves by 0.06°, which means that annealing at 600 °C can improve the crystalline quality and release the inner stress in the films.

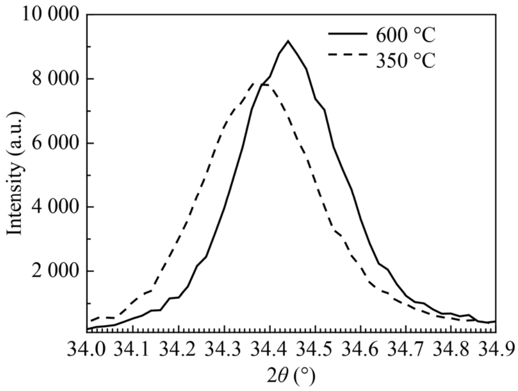
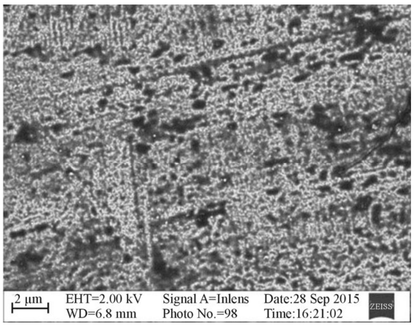
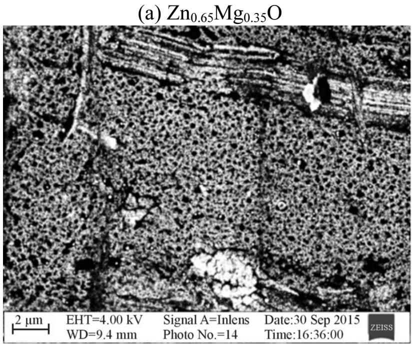



**Fig.3 XRD patterns of $Zn_{0.35}Mg_{0.65}O$ thin films at 350 °C and 600 °C**

In order to investigate the morphology change upon annealing treatment, we choose $x$ values of 0.35 and 0.65 for $Zn_{1-x}Mg_xO$ thin films at annealing temperature of 600 °C, and perform SEM measurement. The results are displayed in Fig.4. We can see that both SEM images of the two $Zn_{1-x}Mg_xO$ films have obvious changes. At annealing temperature of 600 °C, both $Zn_{0.35}Mg_{0.65}O$ and $Zn_{0.65}Mg_{0.35}O$ thin films have a large number of holes, which means that the atomic reconstruction happened and inner stress released. The improvement of crystalline quality can be seen in Fig.3.




(a) $Zn_{0.65}Mg_{0.35}O$




(b) $Zn_{0.35}Mg_{0.65}O$

**Fig.4 SEM images of $Zn_{1-x}Mg_xO$ thin films annealed at 600 °C**

$Zn_{1-x}Mg_xO$ thin films with different $x$ values grown on Si(100) substrate have been investigated by XRD and SEM. XRD results reveal that the $Zn_{1-x}Mg_xO$ thin film is single crystalline structure with $x$<0.3, and when $x$>0.3, the phase separation appears with hexagonal ZnO and cubic MgO structures. The annealing temperature has significant influence on the structure and morphology of $Zn_{1-x}Mg_xO$ thin films with $x$ values of 0.35 and 0.65, the atomic reconstruction happened and the inner stress released in this annealing process, and the crystalline quality can be improved.

## References

[1] C X Cong, B Yao, Q J Zhou and J R Chen, J. Phys. D: App. Phys. **41**, 105303 (2008).

[2] C X Cong, B Yao, G Z Xing, Y P Xie and L X Guan, Appl. Phys. Lett. **89**, 262108 (2006).

[3] Z Vashaei, T Minegishi, H Suzuki, T Hanada, M W Cho and T Yao, J. Appl. Phys. **98**, 054911 (2005).

[4] R. Chandramohan, J. Thirumalai, T. A. Vijayan, S. Valanarasu, S. Elhil Vizhian, M. Srikanth and V. Swaminathan, Adv. Sci. Lett. **3**, 319 (2010).

[5] P.M. Aneesh, M.K. Jayaraj, R. Reshmi, R.S. Ajimsha, L.M. Kukreja, A. Aldrin, F. Rojas, J. Bertomeu, J. López-Vidrier and S. Hernández, J. Nanosci. Nanotechnol. **15**, 3944 (2015).

[6] M.M. Fan, K.W. Liu, Z.Z. Zhang, B.H. Li, X. Chen, D.X. Zhao, C.X. Shan and D.Z. Shen, Appl. Phys. Lett. **105**, 011117 (2014).

[7] I. V. Maznichenko, A. Ernst, M. Bouhassoune, J. Henk, M. Däne, M. Lüders, P. Bruno, W. Hergert, I. Mertig, Z. Szotek and W. M. Temmerman, Phys. Rev. B **80**, 144101 (2009).

[8] J J Yang, Q Q Fang, D D Wang and W H Du, AIP Advances **5**, 047104 (2015).

[9] J J Yang, Q Q Fang, W N Wang, D D Wang and C Wang, J. Appl. Phys. **115**, 124509 (2014).

[10] Z.P. Zhang, H.von Wenckstern and M Grundmann, Appl. Phys. Lett. **103**, 171111 (2013).

[11] Xiaodong Ren, Wei Zi, Qiang Ma, Fengwei Xiao, Fei Gao, Sherry Hu, Yanhua Zhou and Shengzhong Liu, Solar Energy Materials & Solar Cells **134**, 54 (2015).

[12] G. Luka, K. Kopalko, E. Lusakowska, L. Nittler, W. Lisowski, J.W. Sobczak, A. Jablonski and P.S. Smertenko, Organic Electronics **25**, 135 (2015).

[13] Amanpal Singh, Ankush Vij, Dinesh Kumar, P K Khanna, Mukesh Kumar, Sanjeev Gautam and K H Chae, Semicond. Sci. Technol. **28**, 025004 (2013).

[14] Vanita Devi, Manish Kumar, Ravindra Kumar and B.C. Joshi, Ceramics International **41**, 6269 (2015).