Applied Physics Letters

Phase stability of cubic Mg0.55Zn0.45O thin film studied by continuous thermal annealing method

Z. G. Ju, C. X. Shan, C. L. Yang, J. Y. Zhang, B. Yao et al.

Citation: Appl. Phys. Lett. **94**, 101902 (2009); doi: 10.1063/1.3097022
View online: http://dx.doi.org/10.1063/1.3097022
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v94/i10
Published by the American Institute of Physics.

Related Articles

Additional information on Appl. Phys. Lett.

Phase stability of cubic $Mg_{0.55}Zn_{0.45}O$ thin film studied by continuous thermal annealing method

Z. G. Ju,[1,2] C. X. Shan,[1] C. L. Yang,[3] J. Y. Zhang,[1,a] B. Yao,[1] D. X. Zhao,[1] D. Z. Shen,[1] and X. W. Fan[1]

[1]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, No. 16 East South-Lake Road, Changchun 130033, People's Republic of China*

[2]*Graduate School, Chinese Academy of Sciences, Beijing 100039, People's Republic of China*

[3]*Institute of Optoelectronics and Functional Composite Materials, School of Physics and Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China*

(Received 26 November 2008; accepted 17 February 2009; published online 9 March 2009)

The phase stability of cubic $Mg_{0.55}Zn_{0.45}O$ thin film grown by metal-organic chemical vapor deposition was studied through continuous thermal annealing. The crystal quality and surface smoothness were greatly improved after a continuous thermal annealing at 750 °C. It is attributed to the reducing of interstitial Zn by thermal annealing. However, phase segregation occurred when the sample was annealed at a higher temperature (850 °C), which is identified from both x-ray diffraction patterns and optical transmission spectra. © *2009 American Institute of Physics*.
[DOI: 10.1063/1.3097022]

ZnO is a very attractive wide bandgap semiconductor for its potential applications in short-wavelength light-emitting diodes,[1] laser diodes,[2] ultraviolet photodetectors,[3] etc. For the realization of these applications, two important issues have to be raised, one is realizing *p*-type ZnO, which has been studied extensively,[4,5] and the other is the bandgap engineering,[6,7] which is partly fulfilled by $Mg_xZn_{1-x}O$ due to its larger tunable bandgap from 3.37 to 7.8 eV. However, due to the different structure of MgO (cubic) and ZnO (hexagonal), it is really a challenging work to obtain MgZnO thin film with bandgap between 4.3 and 5.0 eV.[8,9] The bandgap of MgZnO has been extended to 4.77 eV by growing metastable cubic MgZnO films in our previous publication.[10] The stability of the metastable thin films will have a huge impact on the performance of the devices fabricated from them, therefore, it is of great significance by studying the phase stability of the MgZnO films. The thermal stability of wurtzite MgZnO has been studied by Ohtomo *et al.*,[11] and it was found that the film kept single hexagonal phase until 1000 °C. Choopun *et al.*[9] reported that the metastable cubic MgZnO thin film can be easily broken by rapid thermal annealing at 750 °C for one minute. However, a systematic study on the phase stability of cubic MgZnO thin film by thermal annealing is still absent. Moreover, thermal annealing can be an effective way to raise the quality of the alloys, and a very successful example is the III-V group alloys GaMnAs annealed at low temperature (about 250 °C).[12,13] It greatly raises the Curie temperature of $Ga_{1-x}Mn_xAs$ to above 110 K, however, this kind of thermal annealing study is rarely found in cubic MgZnO alloys.

In this letter, metastable cubic $Mg_{0.55}Zn_{0.45}O$ film was prepared by metal-organic chemical vapor deposition (MOCVD) at 450 °C, and the as-grown sample was continuously annealed in air from 550 to 850 °C. The phase stability of sample was studied in this process, and the effect of the annealing on the crystal quality and surface morphology of the film was also studied.

The MgZnO thin film was prepared on sapphire substrate in a MOCVD technique. Diethylzinc, biscyclopentadienyl-Mg, and oxygen were employed as the precursors. The growth temperature was fixed at 450 °C and the pressure at 2×10^4 Pa. The as-grown MgZnO film was annealed in air for 30 min with sequential annealing temperature (550, 650, 750, and 850 °C). The composition of the as-grown and annealed MgZnO thin films is measured by an energy-dispersive x-ray spectrometer (EDS). The morphology was examined using a scanning electron microscope (SEM) (HITACHI S-4800). The structure of the $Mg_xZn_{1-x}O$ thin films was evaluated by an x-ray diffraction (XRD) with Cu $K\alpha$ (0.154 nm) line as the radiation source. The transmission spectra were recorded using a Shimadzu UV-3101PC scanning spectrophotometer.

Figure 1(a) shows the XRD patterns of the as-grown MgZnO and the samples annealed at different temperature. We can see that the as-grown MgZnO is crystallized in pure cubic phase with (111) preferred orientation. For the samples annealed at 550 and 650 °C, a very weak diffraction peak (at 34.42°) from ZnO (002) is observed, but when the annealing temperature reaches 750 °C, the ZnO (002) peak completely disappears and only the (111) peak from zincblende phase can be observed. However, after being annealed at 850 °C, the sample shows an obvious (002) diffraction peak (at 34.56°) of wurtzite MgZnO besides the (111) peak. Figure 1(b) shows the full width at half maximum (FWHM) of the (111) diffraction peak of MgZnO thin film as a function of annealing temperature. It can be seen that the FWHM becomes narrower and narrower with increasing annealing temperature, and when the annealing temperature is 750 °C, high quality cubic MgZnO thin film with FWHM of only 0.084° was obtained. When the annealing temperature is up to 850 °C, the FWHM rapidly increases due to phase separation.

Figure 2 shows the transmission spectra of the as-grown MgZnO and those of the sample after being annealed at dif-

[a]Electronic mail: zhangjy53@yahoo.com.cn.

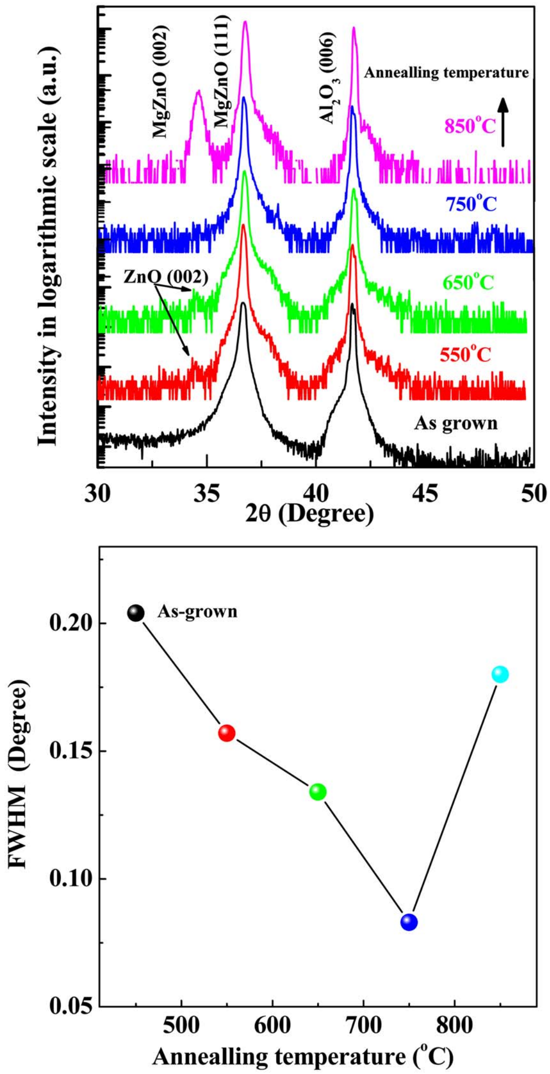

FIG. 1. (Color online) (a) Logarithmic scaled XRD patterns of the as-grown MgZnO and the samples annealed at 550, 650, 750, and 850 °C. (b) FWHM of MgZnO (111) diffraction peak as a function of annealing temperature.

ferent temperature. As shown in Fig. 2, the transmission spectra do not show any changes after the sample is annealed at 550 and 650 °C, which indicates the bandgap of the MgZnO film does not change during the annealing process. When the annealing temperature is 750 °C, the absorption edge becomes sharper, which indicates that the crystallinity of the film has been improved. However, when the annealing temperature is up to 850 °C, the transmission shows two absorption edges at around 360 and 240 nm, indicating that phase separation has occurred in the sample.

Figure 3 shows a typical EDS spectrum of the MgZnO, and the inset shows the Zn content in MgZnO thin films as a function of annealing temperature. As shown from the inset, Zn content in the as-grown MgZnO thin film is 0.45. When the sample was annealed at 550 °C, the Zn content changes to 0.40, and it almost keeps constant after the sample is annealed at 650, 750, and 850 °C. According to the transmission spectra, the bandgap does not vary much in the whole annealing process except at 850 °C but the Zn content decreases significantly after the annealing process. The above phenomenon may be due to the fact that part of redundant Zn is located at interstitial sites, and when the sample was annealed at 550 °C, the redundant Zn tends to escape from the

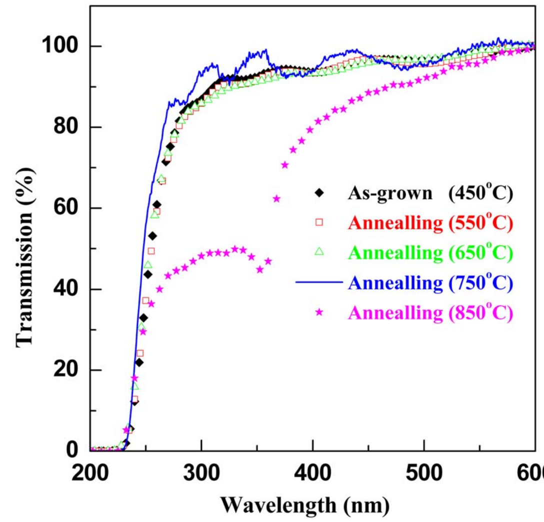

FIG. 2. (Color online) Transmission spectra of the as-grown MgZnO and the samples annealed at 550, 650, 750, and 850 °C.

MgZnO thin film. After the redundant Zn is removed, a relatively stable composition has been achieved.

Figures 4(a)–4(e) show the SEM images of the as-grown MgZnO film and those after being annealed at different temperature. As can be seen from the figures, when the as-grown sample was annealed at 550 °C, there appear some thin hexagonal-shaped sheets on the surface of the thin film. Considering that weak ZnO (002) peak was observed in the XRD pattern of this sample, the hexagons may be ZnO. The formation process can be described as the following scenario. When the as-grown sample was annealed at low temperature (550 and 650 °C), the abundant Zn in the interstitial sites proven by EDS tends to escape from the thin film. When the interstitial Zn arrives at the surface, combining with oxygen in the air, ZnO hexagonal sheets were formed on the surface of the cubic thin film. It is necessary to clarify that only a little part of interstitial Zn has chance to form ZnO sheets and most of it escapes to the air. The decreasing FWHM of XRD pattern of the MgZnO thin films is consistent with such a scenario. It is very similar to the annealing process of

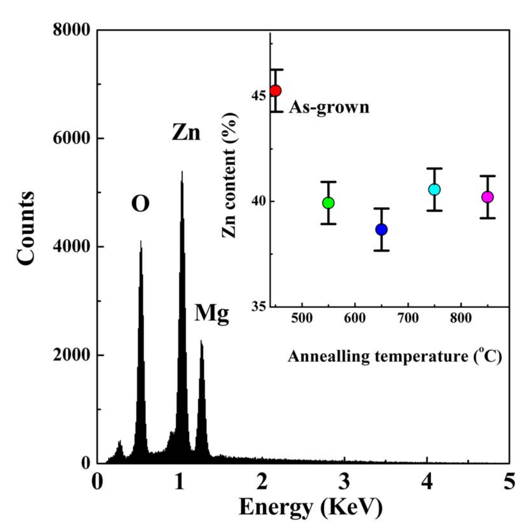

FIG. 3. (Color online) A typical EDS spectrum of the as-grown MgZnO and the samples annealed at 550, 650, 750, and 850 °C. The inset shows Zn content as a function of annealing temperature.

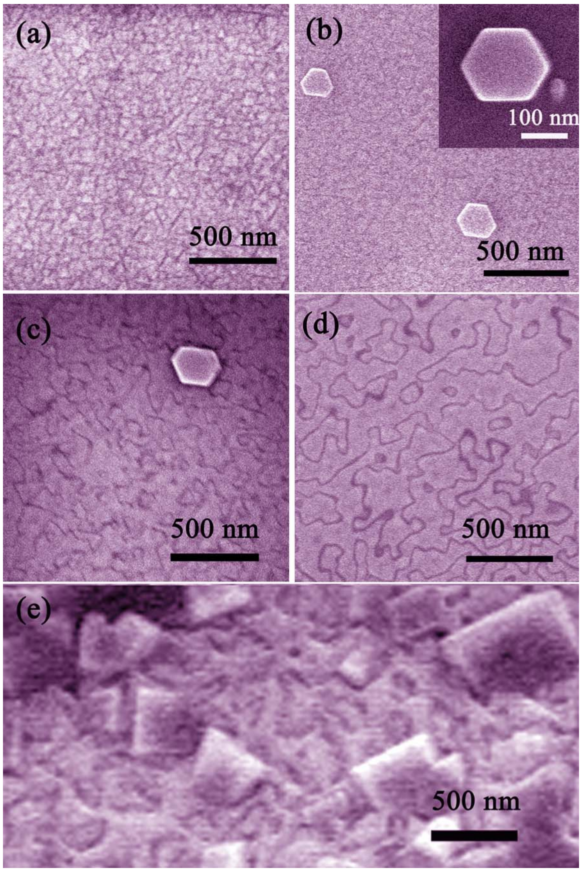

FIG. 4. (Color online) (a) SEM images of the as-grown MgZnO and the samples annealed at (b) 550 °C, (c) 650 °C, (d) 750 °C, and (e) 850 °C.

GaMnAs system. Interstitial Mn diffuses to the surface of the thin films due to thermal annealing, making the point defects greatly reduced, which greatly improve the quality of GaMnAs films.[12,13] However, after being annealed at 750 °C for 30 min, the ZnO hexagonal sheets disappear completely, as shown in Fig. 4(d). The above phenomenon is coincided with the XRD results, in which diffraction peak coming from ZnO appears when the sample is annealed at 550 and 650 °C, whereas it disappears when annealed at 750 °C. It is also found that the surface becomes very smooth when the annealing temperature is 750 °C, which means that ZnO sheets can volatilize completely at 750 °C, as reported by Xue *et al.*[14] However, when the annealing temperature is up to 850 °C, the surface smoothness is seriously destroyed, as shown in Fig. 4(e), which accords well with the occurrence of phase separation as revealed in XRD pattern.

In conclusion, the phase stability of cubic $Mg_{0.55}Zn_{0.45}O$ film has been examined by continuous annealing method. It is found that the film keeps cubic structure when the annealing temperature reaches up to 750 °C. Moreover, annealing below 750 °C can reduce the interstitial Zn greatly, which will accordingly improve the crystal quality of the cubic MgZnO film and promises that devices with better performance may be realized based on the annealed films.

This work is supported by the Key Project of National Natural Science Foundation of China under Grant No. 50532050, the 973 Program under Grant Nos. 2008CB317105 and 2006CB604906, and the Knowledge Innovation Program of the Chinese Academy of Sciences under Grant No. KJCX3.SYW.W01 the National Natural Science Foundation of China under Grant No. 60706021.

[1] S. J. Jiao, Z. Z. Zhang, Y. M. Lu, D. Z. Shen, B. Yao, J. Y. Zhang, B. H. Li, D. X. Zhao, X. W. Fan, and Z. K. Tang, Appl. Phys. Lett. **88**, 031911 (2006).
[2] S. Chu, M. Olmedo, Z. Yang, J. Kong, and J. L. Liu, Appl. Phys. Lett. **93**, 181106 (2008).
[3] S. Liang, H. Sheng, Y. Liu, Z. Huo, Y. Lu, and H. Shen, J. Cryst. Growth **225**, 110 (2001).
[4] L. Dunlop, A. Kursumovic, and J. L. MacManus-Driscoll, Appl. Phys. Lett. **93**, 172111 (2008).
[5] M. Dutta and D. Basak, Appl. Phys. Lett. **92**, 212112 (2008).
[6] A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. Sakurai, Y. Yoshida, T. Yasuda, and Y. Segawa, Appl. Phys. Lett. **72**, 2466 (1998).
[7] Y. Matsumoto, M. Murakami, Z. W. Jin, A. Ohtomo, M. Lippmaa, M. Kawasaki, and H. Koinuma, Jpn. J. Appl. Phys., Part 2 **38**, L603 (1999).
[8] W. I. Park, G.-C. Yi, and H. M. Jang, Appl. Phys. Lett. **79**, 2022 (2001).
[9] S. Choopun, R. D. Vispute, W. Yang, R. P. Sharma, T. Venkatesan, and H. Shen, Appl. Phys. Lett. **80**, 1529 (2002).
[10] Z. G. Ju, C. X. Shan, D. Y. Jiang, J. Y. Zhang, B. Yao, D. X. Zhao, D. Z. Shen, and X. W. Fan, Appl. Phys. Lett. **93**, 173505 (2008).
[11] A. Ohtomo, R. Shiroki, I. Ohkubo, H. Koinuma, and M. Kawasaki, Appl. Phys. Lett. **75**, 4088 (1999).
[12] S. J. Potashnik, K. C. Ku, S. H. Chun, J. J. Berry, N. Samarth, and P. Schiffer, Appl. Phys. Lett. **79**, 1495 (2001).
[13] K. W. Edmonds, P. Bogusławski, K. Y. Wang, R. P. Campion, S. N. Novikov, N. R. S. Farley, B. L. Gallagher, C. T. Foxon, M. Sawicki, T. Dietl, M. Buongiorno Nardelli, and J. Bernholc, Phys. Rev. Lett. **92**, 037201 (2004).
[14] S. B. Xue, H. Z. Zhuang, C. S. Xue, L. J. Hu, B. Li, and S. Y. Zhang, J. Electron. Mater. **36**, 502 (2007).