Structural and optical properties of ZnO films prepared by ion beam sputtering*

WU Shen-jiang(吴慎将)[1,2**], **SU Jun-hong**(苏俊宏)[2], **and WANG Wen-qi**(王稳奇)[1]
1. North Institute of Information Engineering, Xi'an Technological University, Xi'an 710032, China
2. Key Laboratory of Film Technology and Optical Measurement, Xi'an Technological University, Xi'an 710032, China

(Received 13 May 2012)
©Tianjin University of Technology and Springer-Verlag Berlin Heidelberg 2012

Based on the ion beam sputtering deposition technology, ZnO thin films are deposited on the glass substrate. The four-factor and three-level $L_9(3^4)$ orthogonal experiment is used to obtain the best technological parameters of the deposited ZnO thin films, which are the discharge voltage of 3.5 kV, the oxygen current capacity of 8 sccm, the coil current of 8 A and the distance between target and substrate of 140 mm. The purity of the deposited ZnO thin film is 85.77%, and it has good crystallization in orientation. The experimental results show that research and development of the ion beam sputtering source are advanced, and the ion beam sputtering deposition technology can be used to deposit the orientation preferred thin films with good performance.
Document code: A **Article ID:** 1673-1905(2012)06-0449-4
DOI 10.1007/s11801-012-2272-z

ZnO is a semiconductor material with wide bandgap, which has attracted much attention in recent years, and is one of the most promising materials for high-speed ultraviolet photodetectors (UV-PDs)[1–4] due to its direct wide bandgap of 3.37 eV and high exciton binding energy of 60 meV. In addition, ZnO has the high transparency at large carrier concentration and the high radiation hardness. The simplicity of fabrication, low capacitance, low dark currents, good noise suppression, high speed and high sensitivity all contribute to the advantages of using a metal-semiconductor-metal (MSM) structure for photodetectors.

ZnO thin films can be deposited by using a variety of epitaxial growth techniques[5-11]. Since the ion beam sputtering technology has many advantages, such as its little pollution, easy and precise control of the film-forming conditions, and precise adjustment of the beam energy, it is usually considered that the ideal ZnO thin films have high *c*-axis preferred orientation, surface roughness, and fewer defects. In this paper, by using ion beam sputtering source to design the orthogonal experiments, the ZnO thin films are deposited under different process parameters, and the influence of them on the film structures and optical properties is studied.

The ZnO thin films were deposited by ZZX-1100 ion beam sputtering equipment. The device of ion beam sputtering consists of a target, an additional electromagnetic coil which can be adjusted and a composition which leads to polarization of ions. Sputtering efficiency can be changed by changing the discharge voltage and the coil current. The diameter of target is 80 mm, and the purity of the ZnO target is 99.99%.

Clean the substrate to be coated, load it to the substrate holder, and move the substrate holder to the source for substrate cleaning. Vacuumize the chamber to 3.5×10^{-3} Pa. Use the ion beam cleaning source to clean the substrate for 3 min, and put the substrate holder on the source for ion beam sputtering. Inject the working gas of pure oxygen into the chamber to deposite ZnO thin films. Deposit the films, then open the vacuum chamber after cooling, and finally take out the sample.

External conditions which affect the film quality are discharge voltage, gas flow and target-substrate distance. When the discharge voltage is lower than 2.5 kV or above 3.5 kV, the gas flow lower than 6 sccm or above 10 sccm, the ion beam sputtering would produce much ignition and flash, which shows the abnormal work of the ion source. So the levels of discharge voltage are chosen as 2.5 kV, 3 kV and 3.5 kV, and the gas flow levels are 6 sccm, 8 sccm and 10 sccm. To limit the test-bed structure and working space, we choose the target-

* This work has been supported by the National Natural Science Foundation of China (Nos.60978040 and 61205155), and the Science and Technology Projects in Xi'an (No.CXY1015-2).
** E-mail: bxait@xatu.edu.cn

substrate distance as 140 mm, 160 mm and 180 mm. Therefore, in the design of the four-factor and three-level $L_9(3^4)$ orthogonal experiment[12], with the parameters shown in Tab.1, if the refractive index in some groups of the experiment reaches a theoretical value, we believe that these groups can be the better film deposition conditions.

Tab.1 Parameters of the orthogonal experiment

Experiment No.	1	2	3	4	5	6	7	8	9
Discharge voltage (kV)	2.5	2.5	2.5	3.0	3.0	3.0	3.5	3.5	3.5
Gas flowing (sccm)	6	8	10	8	10	6	10	6	8
Target-substrate distance (mm)	140	160	180	180	140	160	160	180	140

Some better groups of thin films are characterized by using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) to get a group of process parameters with a better refractive index, a higher deposition rate and a higher content of 002 (c) direction of ZnO crystals.

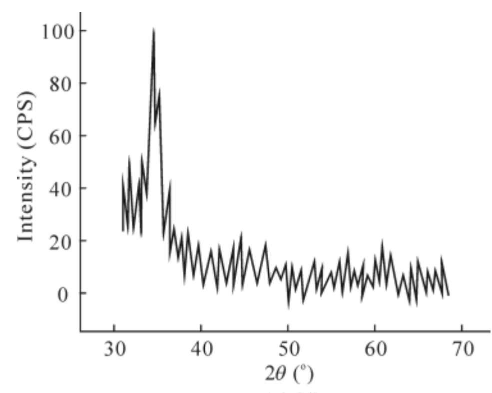
The refractive index of ZnO thin films and the deposition rate shown in Tab.2 are measured by using the Woollam Company's M2000-UI-type wide-spectrum variable angle ellipsometer from the United States.

Tab.2 Analysis of optical properties of ZnO thin films

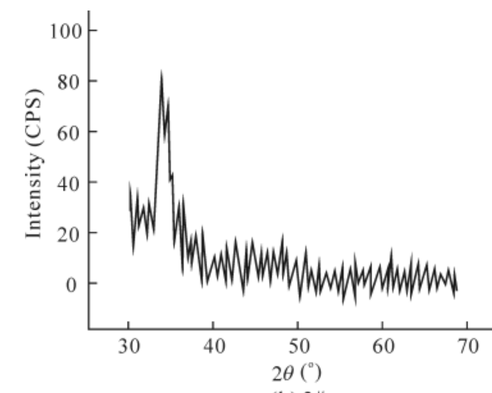
Experiment No.	1	2	3	4	5	6	7	8	9
Refractive index	1.872	1.884	2.025	2.067	1.969	1.943	2.006	2.070	1.984
Deposition rate (nm/min)	2.58	2.83	3.61	3.29	5.23	1.76	7.09	2.33	5.16

The refractive index of ZnO films in the visible range is usually close to a constant of about 2.0. From Tab.2 we know that the samples of Nos.3, 5, 7 and 9 have the better refractive index close to 2.0 and the higher deposition rate, so we take them for XRD test.

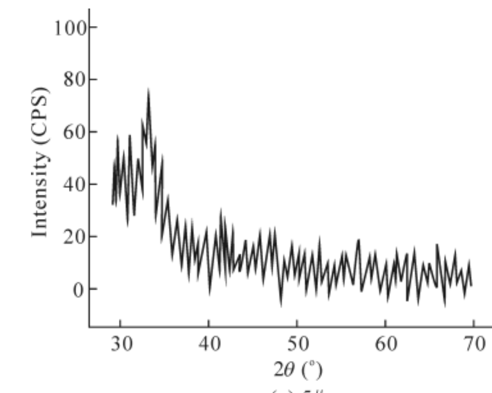
XRD measurements were recorded by the Shimadzu XRD-6000 X-ray diffractometer of Japan, and the samples of 9 #, 3 #, 5 # and 7 # are corresponding to the parameters of the prepared samples Nos.9, 3, 5 and 7, respectively. XRD spectra of four samples are shown in Fig.1, and all samples have a strong peak at about $2\theta = 34^{\circ}$, which are the results of the ZnO (002) crystal surface diffraction. Besides the 002 peak, there is no diffraction peak position. It is shown in Fig.1 that the diffraction intensities of 9 # and 3 # are significantly higher than those of 5 # and 7 #. Therefore, we select the samples 9 # and 3 # to observe the purity of ZnO thin films.



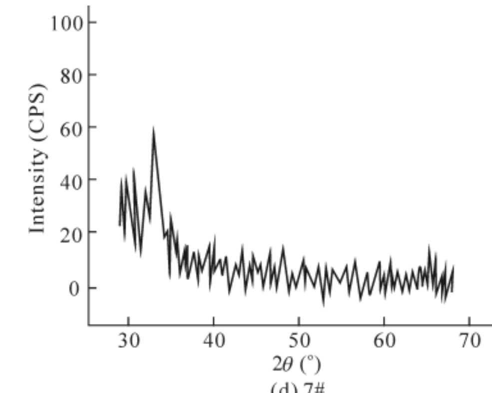
(a) 9#



(b) 3#



(c) 5#



(d) 7#

Fig.1 XRD patterns of ZnO thin films

In XPS experiments, we used the PE Company's PHI5400

X-ray photoelectron spectroscopy of the United States for testing. Before testing, we used ion beam sputtering for 10 min to clean the impurities on the film surface. The results in Fig.2 show that the thin films contain the elements of Zn, O in addition to a small amount of C, which may be caused by indoor air pollution or by vacuum indoor transmission oil. After sputtering, the element of C can be basically eliminated.

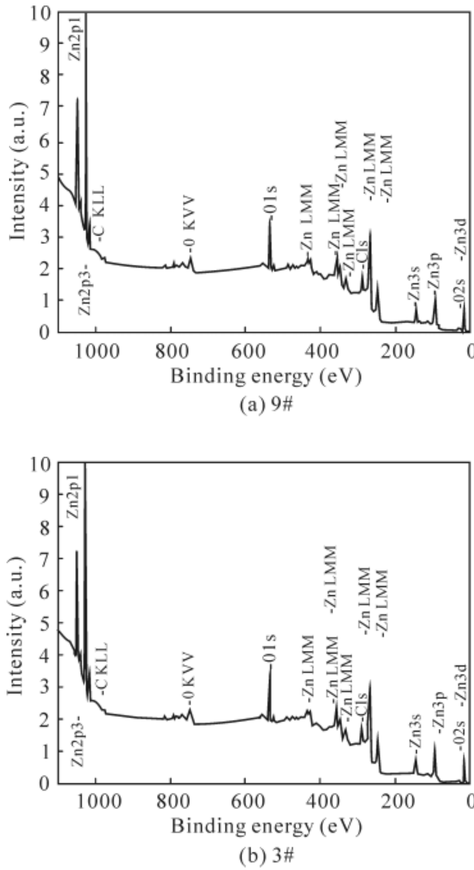


Fig.2 X-ray photoelectron spectra

To make a further high-resolution analysis about the O peaks, we can get the O peak fitting curve shown in Fig.3, and there are two forms of O in the film. One is in the form of Zn_xO_y while the other is a different form. The high binding energy peak is E=532.14 eV, the lattice oxygen valence of Zn-O (ZnO) is -2 price, low binding energy peak is E=530.40 eV, and the relative content of lattice O adsorption of O is about 10% to 30%, which is caused by the growth of ZnO columnar. Although the surface is etched, it is not completely eliminated. The O elements in two forms are shown in Tab.3. In 9# samples, O existing as Zn_xO_y accounts for 85.77%, while the other form is 14.23%. In 3# samples, O existing as Zn_xO_y takes up 77.63% , while the other form is 22.37%.

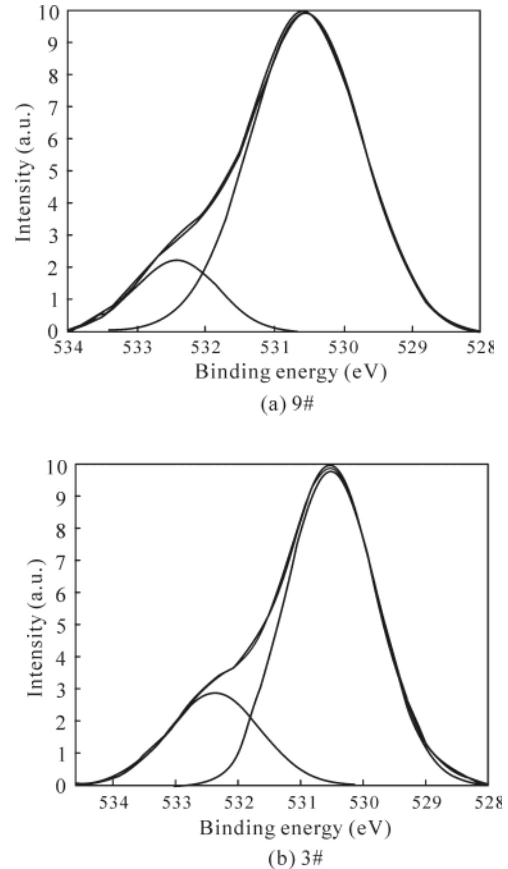


Fig.3 Peak fitting curve of O element

Tab.3 Proportions of two different types of oxygen

Sample	Lattice oxygen O_I(%)	Adsorbed oxygen O_{II}(%)	O_I/O_{II}
3#	77.63	22.37	3.47
9#	85.77	14.23	6.03

We continue to analyze the ratio of x and y in the Zn_xO_y. The Zn and O in the ZnO exist in the forms of Zn_2p_3 and O_1s, respectively. Analyses of Zn and O contents of these two forms of Zn_xO_y can be derived from the ratio of x and y, which are shown in Tab.4. The ratios of Zn and O in the 9# and 3# samples are both close to 1:1. We can consider that the combination of Zn and O is in the form of ZnO. The ZnO content is 85.77% in the 9# samples, and it is 77.63% in the 3# samples.

Tab.4 Relative amounts of Zn_2p_3 and O_{1s} in ZnO thin films

Sample	O_{1s} (%)	Zn_2p_3(%)	Zn:O
3#	50.73	49.27	0.971
9#	50.66	49.34	0.974

By designing a four-factor and three-level $L_9(3^4)$ orthogonal experiment, we use the ion beam sputtering deposition

technology to obtain the best technological parameters for depositing ZnO thin films. The optical quality of ZnO films is studied and we make the XRD analysis on them. We also choose some samples with high diffraction intensity for XPS testing. When the discharge voltage is 3.5 kV, oxygen current capacity is 8 sccm, coil current is 8 A and the target-substrate distance is 140 mm, the refractive index of the deposited ZnO films reaches 1.9836, and the deposition rate is 5.16 nm/min. In the direction of 002(c), the crystallized content reaches 85.77%, and the ratio of Zn and O is 1:1, which demonstrates that these films deposited by ion beam sputtering are precise in qualification orientation in c-axis, high in crystallization, smooth in surface and have fewer defects. They are superior to the films prepared by other means.

References

[1] N. Ait Ahmed, G. Fortas, H. Hammache, S. Sam, A. Keffous, A. Manseri, L. Guerbous and N. Gabouze, Appl. Surf. Sci. **256**, 7442 (2010).

[2] LIU Han-fa and WANG Zhen-huan, Journal of Optoelectronics • Laser **22**, 400 (2011). (in Chinese)

[3] J. H. Liang, H. Y. Lai and Y. J. Chen, Appl. Surf. Sci. **256**, 7305 (2010).

[4] N. L. Tarwal and P. S. Patil, Appl. Surf. Sci. **256**, 7451 (2010).

[5] BAI Yu, LI Xiang-ping and QI Jian-ying, Journal of Optoelectronics • Laser **22**, 878 (2011). (in Chinese)

[6] S. K. Hong, Y. Chen, H. J. Ko, H. Wenisch, T. Hanada and T. Yao, J. Electron. Mater. **30**, 647 (2001).

[7] Liu C. H. and Yan Min, Chem. Phys. Lett. **355**, 43 (2002).

[8] Purica M., Budianu E., Rusu E., Danila M. and Gavrila R., Thin Solid Films **403/404**, 485 (2002).

[9] Lee Y. and Kim H., Jpn. J. Appl. Phys. **40**, 2423 (2001).

[10] Jin-Hong Lee, Kyung-Hee Ko and Byung-Ok Park, J. Cryst. Growth **247**, 119 (2003).

[11] S. Lemlikchia, S. Abdelli-Messacia, S. Lafanea, T. Kerdja, A. Guittoumb and M. Saad, Appl. Surf. Sci. **256**, 5650 (2010).

[12] Xu Junqi, FAN Huiqing, Liu Weiguo and Su Junhong, Opto-Elec. Engineering **35**, 45 (2008).