Front. Optoelectron. 2013, 6(3): 270–274
DOI 10.1007/s12200-013-0326-x

RESEARCH ARTICLE

Influence of substrate temperature on *in situ*-textured ZnO thin films grown by MOCVD

Yajuan ZHENG, Xiangbin ZENG (✉), Xiaohu SUN, Diqiu HUANG

School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, China

Abstract The influence of substrate temperature on microstructure, electrical and optical properties of in situ-textured zinc oxide (ZnO) films fabricated by metal organic chemical vapor deposition (MOVCD) had been investigated. Results indicated that the substrate temperature played a very important role on preparation of ZnO thin film. With the raising of temperature, firstly ZnO crystals were perpendicular to the substrate, then they were grown inclining toward the substrate, finally ZnO crystals grown in layers but not regular. Consequently, ZnO film surface morphology changed from smooth to a pyramid structure and then disappeared little by little. Moreover, it was also found in this study that ZnO film was characterized with high crystallinity, low resistivity (2.17×10^{-2}) and high transmittance ($>80\%$). These results suggested that ZnO thin film is suitable for front electrode of silicon thin film solar cell.

Keywords metal organic chemical vapor deposition (MOVCD), in situ-textured, zinc oxide (ZnO) thin film, temperature

1 Introduction

Transparent conductive oxide (TCO) film is one of the most important components of solar cell, which is the most competitive clean and renewable energy. The TCO material not only need high conductivity and good stability in hydrogen plasma, but also need to be effective to stop the diffusion between metal and silicon (Si). Furthermore, high permeability is necessary for the front electrode of solar cell, and high reflectivity is required as the back electrode [1].

Compared to stannic oxide (SnO_2), indium tin oxide (ITO) and other materials, zinc oxide (ZnO) is the better candidate to be used as TCO film for its low material cost, non-toxic, no pollution, stable performance in hydrogen plasma. Moreover, doped ZnO films have lower resistivity and better electrical stability [2–4]. Currently, ZnO thin film can be prepared by a variety of techniques, such as direct current magnetron sputtering, radio frequency magnetron sputtering, metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), electron beam reactive evaporation (EBRE), spray pyrolysis, pulsed laser deposition (PLD), sol-gel, and so on [5–12]. ZnO can be extensively fabricated to obtain low resistivity, high light transmittance and good stability TCO films in large scale at a relatively low temperature and proper pressure. And the very important reason is that ZnO thin film grown by MOCVD can form an in situ-textured surface just by controlling the temperature of substrate, which can increase the incident light optical path and ignore the corrosion process as well, so reduce the complexity of fabrication and cost of thin film solar cell. Therefore, the preparation of ZnO thin film by MOCVD is competitive in the processes of silicon thin film solar cell. Properties of textured ZnO films grown in situ by MOCVD at different temperatures have been also studied in this paper.

2 Experimental methods

In this experiment, Diethylzinc (DEZn) and water vapors had been used as reaction gases which were carried by Argon (Ar), and ZnO thin films were deposited on glass substrate (230 mm × 230 mm) by MOCVD in a vertical way. Although the dimension of applied substrate (230 mm × 230 mm) is relatively large, but depositing film in large scale is one of the properties of MOCVD, and this is the dimension fabricated ZnO film, and it was cut into small pieces when tested. ZnO films could be deposited

Received March 25, 2013; accepted May 16, 2013

E-mail: eexbzeng@163.com

well-distributed in low temperature and in large scale, and this is one of the advantages for MOCVD used in fabricating solar cells. As reaction gases flow rates, working pressure and temperature of substrate all have important influence on preparation and characteristics of ZnO thin film, we optimized the parameters of depositing process after a lot of experiments, such as the flow rates of DEZn, water vapors and the working pressure, and the optimized values are 100 sccm, 55 sccm and 130 Pa respectively. For temperature, our experiments showed that ZnO film is very sensitive at 170°C, and it can be compatible with the process of thin film solar cells, so we chose the temperature changing from 160°C to 190°C. As far the thickness of ZnO, as the temperature changing range was narrow, the thickness of ZnO film did not change much, an average thickness has been selected in this study, and the film thickness was about 350 nm.

X-ray diffraction (XRD, Bruker D8Focus, CuK_α, $\lambda = 0.15406$ nm) analysis was performed to investigate the crystallographic structure of ZnO films. Scanning electron microscope (SEM, HITACHI S-4800) and atomic force microscope (AFM) were used to display the films' surface morphologies. Electrical parameters were measured by Hall measurement after Al electrode was deposited on the ZnO film. The optical transmittance of ZnO films was evaluated by 7-SCSPEC solar cell spectral performance testing system, and testing wavelength was between 300 and 1100 nm. Spectroscopic ellipsometry (SOPRA GES-5E) was used to measure the film thickness.

3 Results and discussion

3.1 ZnO structural properties

ZnO is a wide direct band gap semiconductor, and its surface energy varies with different crystal surface. Therefore, films' structure changes with the substrate temperature. We studied the XRD pattern of ZnO films which were grown in different temperatures, and the results were shown in Fig. 1. A metastable cubic phase with the rocksalt (NaCl) structure occurred when the pressure increased to 9.8 GPa (at 300 K). And zincblende structure occurred when the substrate was cubic. ZnO generally appeared as hexagonal wurtzite phase that one unit cell contained 2 molecules. The zinc atoms were surrounded by oxygen atoms in a nearly tetrahedral configuration and the oxygen atoms were surrounded by zinc atoms in a nearly tetrahedral configuration as well. Furthermore, one Zn-O axis was perpendicularly and its distance was smaller than that for the other three neighboring oxygen atoms [13]. As temperature was low (160°C), a sharp peak for ZnO (002) and weak peaks for (100) and (110) were shown in Fig.1, it was suggested that the sample was highly crystallized and highly *c*-axis oriented, the film were smooth. With the temperature

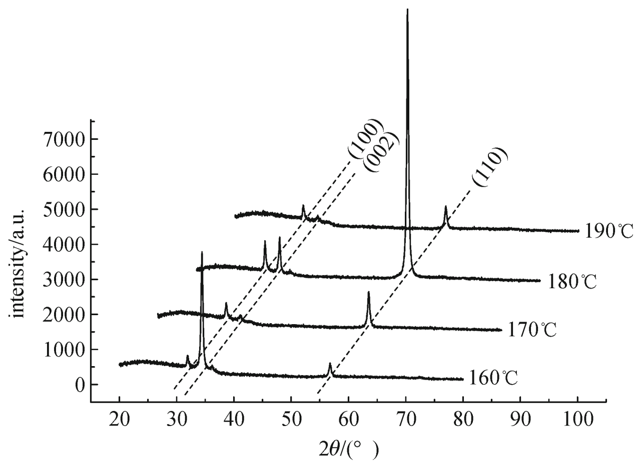

Fig. 1 XRD data as function of substrate temperature

increasing, the intensity of the (002) diffraction peak was weaken down, but (110) peak was enhanced, which indicated that the ZnO molecules were grown no more *c*-axis oriented. When the temperature reached 180°C, the intensity of (110) peak reached the strongest, and (100) and (002) peaks also had a little increase. Meanwhile c-axis was no longer perpendicular to the substrate but inclined toward the substrate. The ZnO film formed a pyramid structure that could increase the absorption of sun light while it was used as solar cell's front electrode. As the temperature increased further, the intensity of all peaks weaken down, so the crystallinity of film reduced. Hence, a textured structure ZnO film could be fabricated at 180°C without any more processes.

The surface morphology of ZnO thin film could be observed directly by SEM. The results are shown in Fig. 2. At 160°C, globular particles of ZnO were very small and closely packed, and the film was relatively smooth (Fig. 2(a)). As the temperature increased to 170°C, ZnO particles shape became irregular and many conical particles appeared. At the same time, the size became larger and no longer consistent (Fig. 2(b)). When the temperature increased up to 180°C, the grains were grown larger, uniform, and tightly packed. And more importantly, the grains were pyramid structure and the film was textured structure (Fig. 2(c)). While as the temperature continued rising, the pyramid structure gradually disappeared and was replaced by a rock structure, of which surface became more flat (Fig. 2(d)). According to these results shown in Fig. 2, the best temperature for *in situ*-textured ZnO thin films was 180°C.

The results of XRD and SEM consistently suggest that the temperature of substrate has great influence on the growing of ZnO film, and at 180°C, high crystallinity and textured structure ZnO film could be obtained. Surface morphology of ZnO film grown at 180°C could be shown very clearly by AFM in Fig. 3, in which well-distributed textured structure could be seen clearly. Textured structure

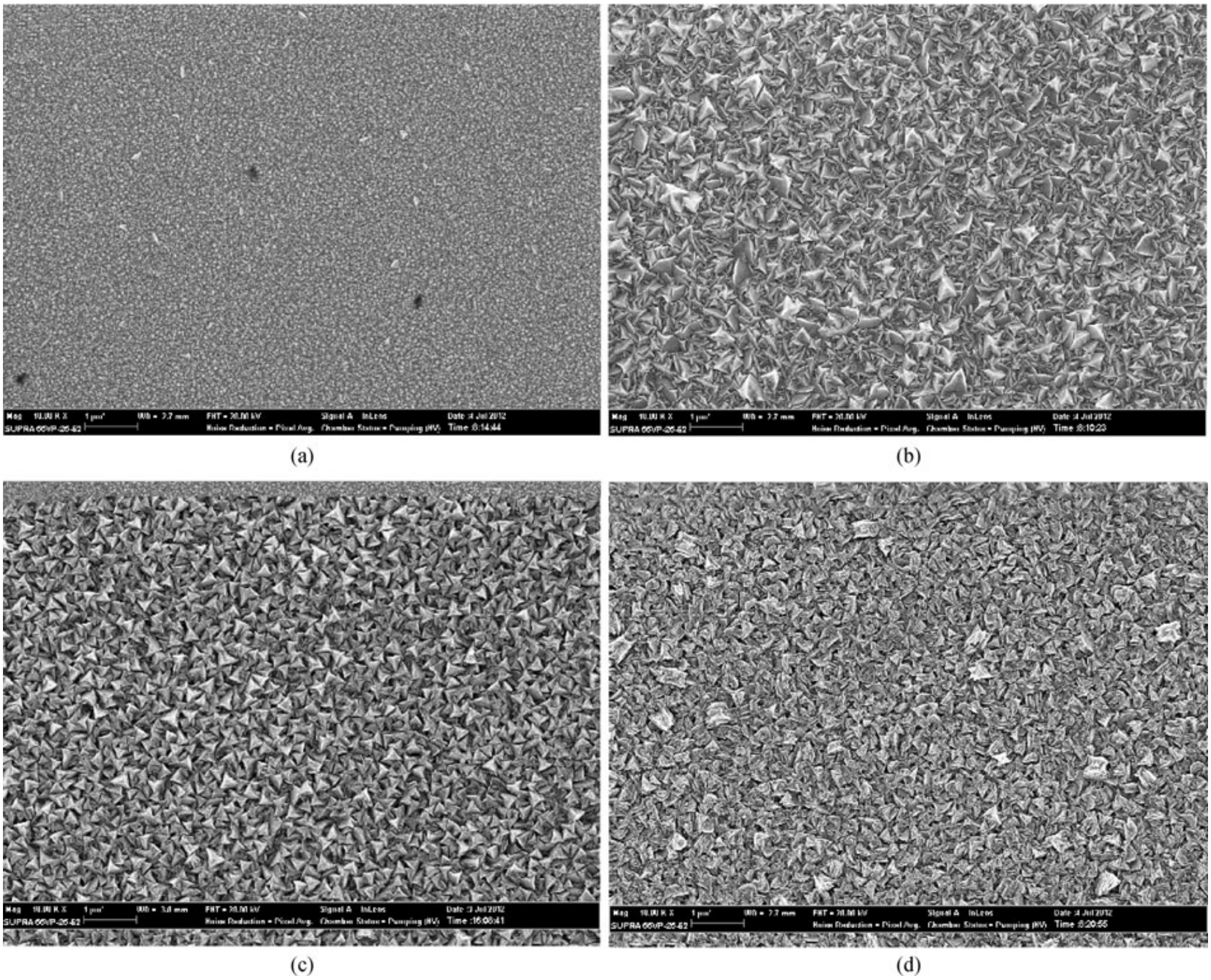

Fig. 2 SEM results of ZnO thin film at different temperatures: (a) 160°C; (b) 170°C; (c) 180°C; (d) 190°C

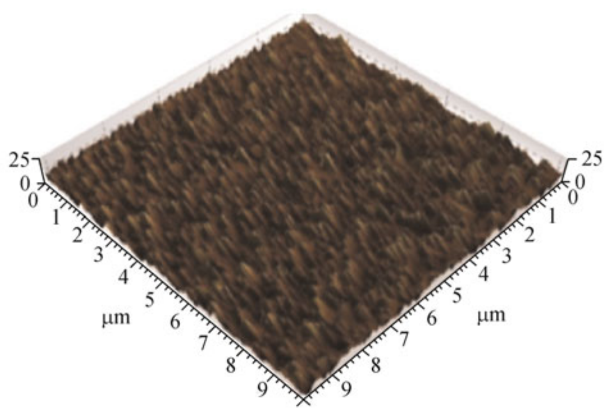

Fig. 3 AFM result of ZnO film grown at 180°C

ZnO film can be used as the front electrode of solar cell. And it can improve light scattering, and increase the incident light optical path. Consequently, the absorption of light in the cell increases a lot, and then the efficiency of the cells is improved. Therefore, ZnO film with light trapping structure can be prepared with MOCVD directly by controlling test condition without corrosion technology.

3.2 Electrical and optical properties

ZnO is a compound semiconductor with a direct and wide band gap of 3.37 eV. Figures 4(a)–4(c) respectively show the changes of resistivity (ρ), electron mobility (μ) and carrier concentration (n) of ZnO films prepared at different temperatures. Combined with XRD analysis, it was found that as the temperature was 160°C, the grains were small, closely packed and the number of interface was large which resulted in electrons in athletic process by scattering were strong and carrier mobility was small. On the other hand, because ρ was equaled to $1/nq\mu$, even if carrier concentration was not small, the resistance rate was still relatively high. When the temperature increased, the grains became bigger and the number of interface became less, then electrons in athletic process by scattering were weak, and carrier mobility was large and the resistance rate decreased. As the temperature reached 180°C, the grains

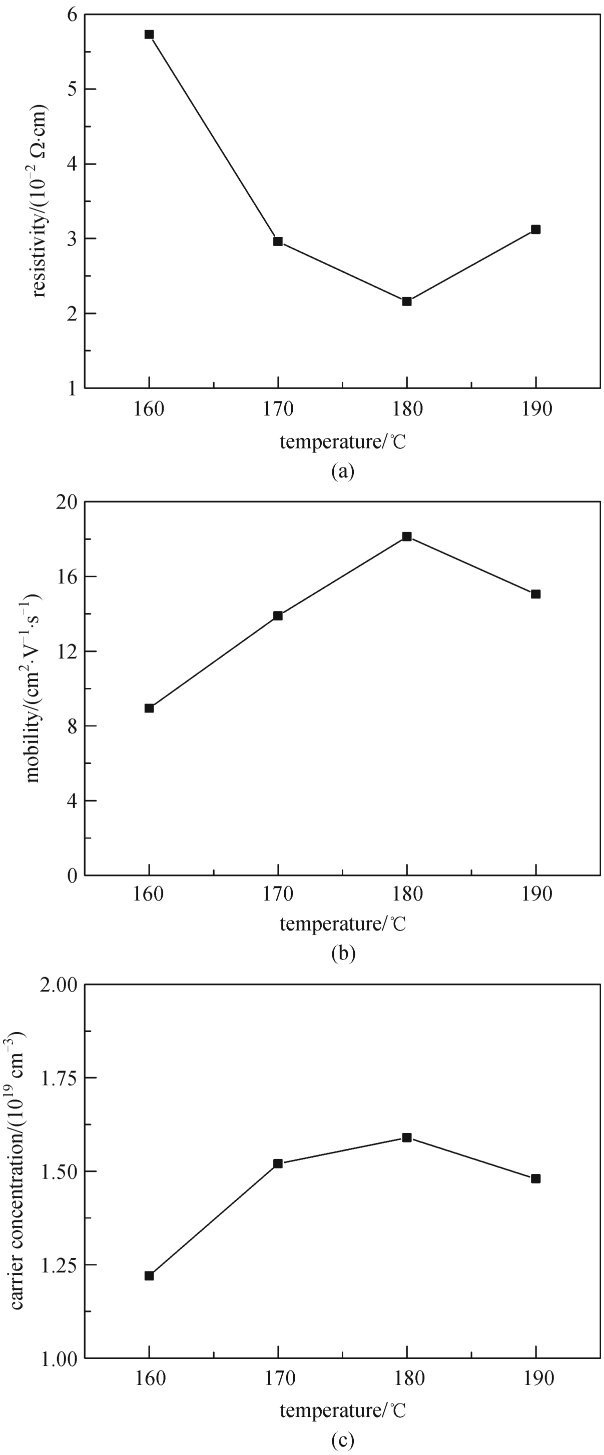

Fig. 4 Resistivity (a); mobility (b); and carrier concentration (c) of ZnO thin films at different substrate temperatures

got larger, uniform, tightly packed and less defects, and the film had the minimum resistivity. When the temperature was higher than 180°C, the film crystallization rate declined and large numbers of defects appeared. Concurrently, the carrier mobility and the carrier concentration

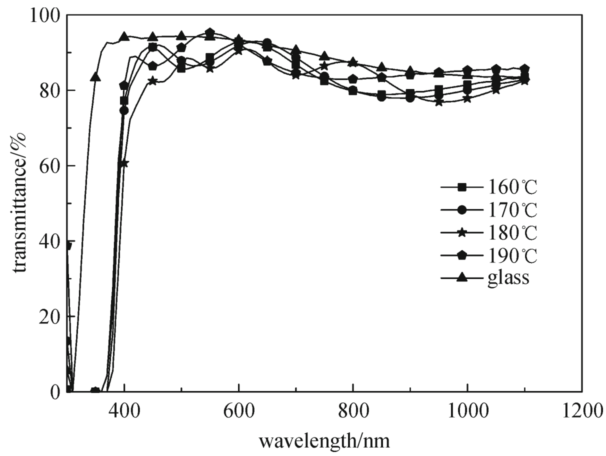

Fig. 5 Transmittance at different temperatures

decreased. As a consequence, ZnO film resistivity became bigger.

When ZnO thin film is used as the front electrode of solar cells, both low resistivity and good light permeability are required. Figure 5 shows changes of optical transmittance of the films fabricated at different temperatures. It can be found that in the range of infrared and visible light, optical transmittance decreased with temperature increase, but it was all above 80% which is suitable for thin film solar cell.

4 Conclusions

Structure, electrical and optical properties of ZnO films fabricated on different temperatures by MOCVD had been studied. The results suggested that the preparation of ZnO thin film at 180°C had high crystallinity, low resistance and high transmittance. Furthermore, the ZnO thin film got *in situ*-textured structure without any processes. These zinc oxide thin films can be used as the front electrode of silicon thin film solar cell to improve its efficiency.

Acknowledgements This work was supported by Supporting Technology Project of Ministry of Education of China (No. 62501040202). The authors would like to thank all members of the thin film group at the Photonic and Information System Integration Institute for their support of this work and helpful discussion. The authors also thank Analytical and Testing center of Huazhong University of Science & Technology for their valuable suggestions and help for the samples characterizations.

References

1. Müller J, Rech B, Springer J, Vanecek M. TCO and light trapping in silicon thin film solar cells. Solar Energy, 2004, 77(6): 917–930
2. Zou D C, Wang D, Chu Z Z, Lv Z B, Fan X. Fiber-shaped flexible solar cells. Coordination Chemistry Reviews, 2010, 254(9–10): 1169–1178

3. Dagkaldiran Ü, Gordijin A, Finger F, Yates H M, Evans P, Sheel D W, Remes Z, Vanecek M. Amorphous silicon solar cells made with SnO_2:F TCO films deposited by atmospheric pressure CVD. Materials Science and Engineering B, 2009, 159–160: 6–9
4. Manavizadeh N, Boroumand F A, Asl-Soleimani E, Raissi F, Bagherzadeh S, Khodayari A, Rasouli M A. Influence of substrates on the structural and morphological properties of RF suppered ITO thin films for photovoltaic application. Thin Solid Films, 2009, 517 (7): 2324–2327
5. Wang X J, Zeng X B, Huang D Q, Zhang X, Li Q. The properties of Al doped ZnO thin films deposited on various substrate materials by RF magnetron sputtering. Materials in Electronics, 2012, 23(8): 1580–1586
6. Stowell M, Müller J, Ruske M, Lutz M, Linz T. RF-superimposed DC and pulsed DC sputtering for deposition of transparent conductive oxides. Thin Solid Films, 2007, 515(19): 7654–7657
7. Pan M, Fenwick W E, Strassburg M, Li N, Kang H, Kane M H, Asghar A, Gupta S, Varatharajan R, Nause J, El-Zein N, Fabiano P, Steiner T, Ferguson I. Metal-organic chemical vapor deposition of ZnO. Journal of Crystal Growth, 2006, 287(2): 688–693
8. Wang S P, Shan C X, Yao B, Li B H, Zhang J Y, Zhao D X, Shen D Z, Fan X W. Electrical and optical properties of ZnO films grown by molecular beam epitaxy. Applied Surface Science, 2009, 255(9): 4913–4915
9. Al Asmar R, Ferblantier G, Sauvajol J L, Giani A, Khoury A, Foucaran A. Fabrication and characterization of high quality ZnO thin films by reactive electron beam evaporation technique. Microelectronics Journal, 2005, 36(8): 694–699
10. Bacaksiz E, Aksu S, Yilmaz S, Parlak M, Altunbas M. Structural, optical and electrical properties of Al-doped ZnO microrods prepared by spray pyrolysis. Thin Solid Films, 2010, 518(15): 4076–4080
11. Bruncko J, Vincze A, Netrvalova M. Study of ZnO layers growth by pulsed laser deposition from Zn and ZnO targets. Vacuum, 2009, 84 (1): 162–165
12. Kim Y S, Tai W P. Electrical and optical properties of Al-doped ZnO thin films by sol-gel process. Applied Surface Science, 2007, 253(11): 4911–4916
13. Wu Y B. Deposition of ZnO and Al Depoed ZnO Films by Magnetron Sputtering and Fabrication of MSM Ultraviolet Photodetector. Dissertation for the Doctoral Degree. Xiamen: Xiamen University, 2009