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Effect of Electron Beam Annealing Duration on the Properties of Zno Thin Films

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Abstract. The effect of electron beam (EB) annealing duration on the properties of pure ZnO thin films was studied. Pure ZnO precursor films prepared by sol-gel spin coating method were directly annealed by EB for different duration from 20 s to 480 s. The structural, optical and electrical properties were investigated. XRD patterns show (002) preferential growth for all the ZnO films. SEM results reveal that the average grain size changes from ~10 nm to ~70 nm with the increase of annealing duration and AFM results show the surface RMS roughness is less than 3 nm. The optical transmittance spectra present the absorption edge of the films is at about 380 nm and the average transmittance is more than 85% in visible region. It's exciting to find that the ZnO film annealed for only 120 s exhibits resistivity $2 \times 10^{-2} \Omega$ cm and carrier concentration as high as 5.5×10^{19} cm⁻³, which shows an advantage of EB annealing in the preparation of ZnO transparent conductive films.

1. Introduction

Tin-doped indium oxide (ITO), used in solar cells [1,2], thin film transistors (TFTs) [3,4] and lightemitting diodes (LED) [5,6] during the past 50 years and today [7], is the most important transparent conductive oxides (TCO). Unfortunately indium is toxic and expensive. Zinc oxide (ZnO) becomes one of the most promising candidate of ITO because it presents some advantages such as nontoxicity, low cost, high thermal and chemical stability. ZnO is a native n-type semiconductor with a direct wide band gap of 3.36 eV [8], which makes it conductive and transparent in visible range. The conductivity of pure ZnO can be further improved by increasing oxygen vacancy or doping with IIIA (B, Al, Ga, in), IIIB (Sc, Y, La), IVA (Ti, Zr, Hf) and IVB (Si, Ge, Sn) elements and non-metal anions, such as Cl and F [7].

Many methods, such as magnetron sputtering [9], atomic layer deposition (ALD) [10], pulsed laser deposition (PLD) [11], chemical vapor deposition (CVD) [12] and sol-gel method [13], have already been utilized to prepare ZnO thin films. Among the synthesis methods, sol-gel process is widely studied due to the easy control of film composition and low cost for fabrication of large-area film [14]. Nevertheless, the main shortcoming of sol-gel is the relatively long post annealing process. It usually takes several hours to anneal the precursor and the resistivity of pure ZnO thin film is higher, up to 101 or 102 Ω cm [15-18]. Research results find that the preparation method and post annealing process

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play an important role in the electrical characteristic of ZnO films [19]. And EB irradiation proved to be an effective way to improve the optical-electrical properties of TCO film. For example, the opticalelectrical properties of Au/ITO and ITO/Au/ITO multilayer thin films deposited by EB evaporation were enhanced by applying EB irradiation [20]. The resistivity of doped and undoped ZnO films irradiated by EB decreased [16, 17]. In addition, our previous work [21] has demonstrated that EB annealing combined with sol-gel method is a new way to prepare ZnO transparent conductive films. The pure ZnO thin film annealed for 5 min with carrier concentration 6.30×1019 cm-3 and resistivity $1.57 \times 10-2$ Ω cm was obtained. High energy electrons are used to heat the sample during the EB annealing process. The surface temperature of the sample rises rapidly when exposed to EB, and falls quickly to the room temperature when EB exposure stops [22]. What's more, EB annealing process is conducted in vacuum and the cooling rate is quick, which is important to prepare ZnO with high electrical performances. Annealing in vacuum atmosphere can increase the concentration of oxygen vacancies and rapid cooling process can help to stop the diffusion of oxygen back into the ZnO film [23-25]. Hence the electrical properties of ZnO film can be improved. Here we mainly study the effect of EB annealing duration especially ultrashort time on the properties of pure ZnO thin films.

2. Experiments

2.1. Films preparation

The preparation process of ZnO precursor film in this experiment has been described in detail elsewhere [21]. Briefly the pure aged 0.75 M sol solution was deposited over substrates, $10 \times 10 \times 0.5$ mm³ in size, via spin coating at spin speed of 600 rpm for 6s and 3000 rpm for 30 s. To remove the organic residues the coated substrates were dried on a hotplate at 300 °C for 10 min. The above steps including deposition and drying were repeated 9 times in order to obtain a reasonable thickness. Then the precursor films were directly annealed in an EB annealing equipment, EBW-3H, with vacuum pressure 4.0×10^{-3} Pa, accelerating voltage 10 kV, beam current 0.7 mA and beam diameter 2 cm. The annealing duration varied from 20 s to 480 s. What needs illustration is that the time zero is the moment when the precursor film is exposed to EB.

2.2. Characterization

Spectroscopic ellipsometer (SE 850 DUV), X-ray diffraction (XRD, Bruker D8 ADVANCE), atomic force microscope (AFM, Bruker Nano Inc. ICON2-SYS) and scanning electron microscope (SEM, CARL ZEISS SIGMA) were used to mainly study the structural properties of the ZnO films. UV-Vis spectrophotometer (Varian Cary 5000) and Hall Effect measurements (HALL8800) were used to investigate the optical and electrical properties of the ZnO films respectively.

3. Results and Discussion

3.1. Structural properties

Figure 1 shows the SEM images of ZnO films annealed for different duration. It can be seen that all the films consist of continuous nanometer-sized grains and the grains connect closely. And all the films show typical pores and voids [26, 27] which formed when the gas overflow during the annealing process. The average grain size increases from ~10 nm to ~70 nm with the expansion of annealing duration, which is because the precursor films can acquire enough energy from the incident EB and have enough time to grow into larger grains when the annealing duration expands. The larger grains can further help to fill the holes in the surface and that's why the film annealed for 480 s reveals relative large grains and small number of holes.

The AFM images of ZnO films are shown in Figure 2. And the surface roughness as manifested by root-mean-square (RMS) values was analyzed, as shown in Table 1. The small values indicate that the surface of the ZnO thin films is smooth. Furthermore, owing to the grain growth the surface RMS

roughness obviously increases with the expansion of annealing duration, which is also consistent with the SEM images shown in Figure 1.



Figure. 1 SEM images of ZnO thin films.



Figure. 2 AFM images of ZnO thin films.

Table. 1	The surface	e RMS roi	ughness	of ZnO	thin fil	lms anne	aled for	different	time

	20 s	60 s	90 s	120 s	240 s	360 s	480 s
R_{q} (nm)	1.48	1.72	2.08	2.16	2.23	2.53	2.83

Figure 3 shows the XRD patterns of all the ZnO films in the range of 30 to 60° . The crystallographic structure of all the films are confirmed to be Wurtzite ZnO. The major peaks are indexed to be from (100), (002), and (101) planes and the ZnO thin films grow towards the c-axis lattice orientation. It's easy to find that the intensity of the (002) orientation increase notably as the annealing duration expands, which indicates the crystallinity of the ZnO films is enhanced [18]. As annealed for longer time, the films can obtain enough energy to reach crystallizing temperature and gain more time to grow into high quality grains.

The grain size along the c-axis, the lattice constant c for the (002) orientation and the stress in the plane of all the films were calculated by the following three formulas respectively [26, 28]:

$$D = \frac{0.9\lambda}{W\cos\theta} \tag{1}$$

$$c = \frac{\lambda}{\sin \theta} \tag{2}$$

$$\sigma = -233 \frac{c - c_0}{c_0} \tag{3}$$

Where *D* is the average dimension of the crystallites normal to the reflecting planes, λ is the X-ray wavelength ($\lambda = 0.154$ nm, Cu K α), θ is Bragg angle of (002) peak, *W* is FWHM value, c_0 is the lattice constant of power ZnO ($c_0 = 0.5205$ nm) and *c* is the lattice constant of ZnO films in the experiment.

The changes of 2θ , *D*, *c* and σ of ZnO thin films with different annealing duration are presented in Figure 4. As shown in Figure 4 (a) the value of (002) diffraction peak 2θ is larger than 34.421 ° (value for ZnO Ref. Pattern: JCPDS 75-0576), which can be attributed to some factors such as interstitial defects and lattice strain [29]. The value of *D* ranges from 10 nm to 65 nm shown in Figure 4 (b), which is almost consistent with the SEM images presented in Figure 1.The positive value of σ shown in Figure 4 (d) implies that the crystallites are in a state of tensile stress and $c < c_0$ as shown in Figure 4 (c). The stress in the film is the combination of the intrinsic stress and the extrinsic stress. The intrinsic stress is closely in correlation with defects and lattice distortions in the crystal and the extrinsic stress is commonly considered to come from the mismatch of thermal expansion coefficients between the film and substrate [30].



Figure. 3 XRD patterns of ZnO thin films



Figure. 4 The changes of 2θ (a), c (b), D (c) and σ (d) of ZnO thin films with annealing duration.

3.2. Optical properties

Figure 5 shows the optical transmittance spectra of ZnO films in the wavelength range of 200-800 nm and the inset shows the average transmittance in visible region. It can be seen that all the films present sharp absorption edges at about 380 nm and relatively high average transmittance in visible region, over 85%. The average transmittance of the films increases with annealing duration, which is closely related to the crystallinity and the surface roughness of the films. When the annealing duration is less than 120 s, the films crystallize better and the grains grow larger as annealing duration expands. The number of grain boundary reduces and so does the grain boundary scattering of photons. As a result the transmittance increases rapidly. When annealing duration changes from 120 s to 360 s, the larger whole size and surface roughness of the films increase the scattering of photons, which leads to the slow increase of the average transmittance. And the ZnO film annealed for 480 s presents the highest average transmittance close to 94% due to its large grains and the small number of holes.

To analyze the optical band gap of the ZnO thin films, the absorption coefficient, α of the films is firstly calculated [27, 31]

$$\alpha = -\ln\left(T\right)/d\tag{4}$$

Where T is the normalized optical transmittance obtained from optical transmittance spectra. D is the film thickness, 100 nm, measured by spectroscopic ellipsometer.

And then the optical band gap, *Eg*, can be gained by using the following Tauc's model:

$$\left(\alpha h\upsilon\right)^{\frac{1}{n}} = C\left(h\upsilon - E_g\right) \tag{5}$$

Where *h* and *v* are the Planck constant and frequency of the radiation respectively. *N* represents the nature of the transition. *C* is a constant. For ZnO the values of *n* and *C* are 0.5 and 1 respectively. Finally the values of optical energy gap can be obtained by extrapolating the linear part to $\alpha = 0$ using Eq. (5), as shown in Figure 6.



Figure. 5 The optical transmittance and average



Figure 6. $(Ahv)^2$ -hv curves of ZnO thin films. Transmittance in visible region of ZnO thin films.

As annealing duration expands, the band gap of the films increases from ~ 3.26 eV to ~ 3.29 eV shown in Figure 6. In nanocrystalline, the ZnO film with larger grain presents wider band gap due to the dimensional effect [32-35]. In addition, based on the Burstein-Moss model, the higher carrier concentration in ZnO film can widen the optical band gap due to the lowest levels of the conduction band being filled with charge carriers in semiconductors [36]. The carrier concentration of the films will be discussed in next part.

3.3. Electrical properties

The changes of the carrier concentration (*n*), Hall mobility (μ), and resistivity (ρ) of ZnO thin films annealed for different duration are shown in Figure 7. It is obvious that the decrease in film resistivity results from an increase in both carrier concentration and mobility. The mobility is significantly determined by the scatterings of impurity and grain boundary. When the annealing duration is less than 120 s, the grains in the films grow larger as annealing duration expands. Thus the mobility increases rapidly due to the decrease of grain boundary scattering. When the annealing duration is more than 120 s, the increase of impurity scattering like holes and the decrease of grain boundary scattering may reach a balance. So the mobility remains almost unchanged at a high level.

It's worth noting that the ZnO films annealed for more than 120 s present resistivity $\sim 2 \times 10^{-2} \Omega cm$ and carrier concentration $\sim 5.5 \times 10^{19} cm^{-3}$, which may be closely related to the characteristics of EB annealing. Annealing in vacuum contributes to the production of oxygen vacancies [23] and the oxygen vacancies hardly decrease in the rapid cooling process [37]. In the experiments here, with the

expansion of annealing duration the number of oxygen vacancies increase and became saturated when annealing duration is more than 120 s. Thus the carrier concentration increases firstly and remains at a higher value later.



Figure 7. The carrier concentration, Hall mobility, and resistivity of ZnO thin films annealed for different duration.

4. Conclusion

Based on the successful combination of sol-gel spin coating method and EB annealing, the effect of EB annealing duration, from 20 s to 480 s, on the properties of the ZnO films was studied. The results show that the crystallization of ZnO films is enhanced and grains grow larger with the expansion of annealing duration. The film annealed for 480 s presents the highest transmittance close to 94% due to less scattering of photons. What's more, it's surprising to find that the ZnO film annealed for only 120 s exhibits resistivity $2 \times 10^{-2} \Omega cm$ and carrier concentration $5.5 \times 10^{19} cm^{-3}$, which reveals that EB annealing is an effective method to prepare ZnO transparent conductive thin films.

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References

- [1] Hussein Awada, Giorgio Mattana, Aurélien Tournebize, Laurent Rodriguez, Delphine Flahaut, Luc Vellutini, Christine Lartigau-Dagron, Laurent Billon, Antoine Bousquet, Sylvain Chambon, Organic Electronics 57(2018)186-193.
- [2] Huafei Guo, Kezhi Zhanga, Xuguang Jia, Changhao Ma, Ningyi Yuan, Jianning Ding, Optik 140(2017)322-330.
- [3] Jun Li, Xing-Wei Ding, Jian-Hua Zhang, Wen-Qing Zhu, Xue-Yin Jiang, Zhi-Lin Zhang, Curr. Appl. Phys. 14(2014)1036-1040.
- [4] Hyun Jong Kim, Byung Sang Song, Won-Ju Cho, Jong Tae Park, Microelectron. Reliab. 76-77(2017)333-337.
- [5] H. L. Hao, L. K. Wu, W. J. Chung, Y. Zhang, W. Z. Shen, Microelectron. Reliab. 55(2015)2263-2268.
- [6] Sang-Mok Lee, Hyun-Woo Koo, Tae-Woong Kim, Han-Ki Kim, Surf. Coat. Tech. 343(2018)115-120.
- [7] Arindam Mallick, Durga Basak, Prog. Mater. Sci. 96(2018)86-110.
- [8] Samia Tabassum, Eiji Yamasue, Hideyuki Okumura, Keiichi N Ishihara, Appl. Surf. Sci. 377(2016)355-360.
- [9] M. R. Alfaro Cruz, O. Ceballos-Sanchez, E. Luévano-Hipólito, L. M. Torres-Martínez, Int. J. Hydrogen Energ. 43(2018)10301-10310.

- [10] S. I. Boyadjiev, V. Georgieva, R. Yordanov, Z. Raicheva, I. M. Szilágyi, Appl. Surf. Sci. 387(2016)1230-1235.
- [11] M. S. Al-Assiri, M. M. Mostafa, M. A. Ali, M. M. El-Desoky, Superlattice. Microst. 75(2014)127-135.
- [12] Xiangyang Duan, Guangde Chen, Lu'an Guo, Youzhang Zhu, Honggang Ye, Yelong Wu, Superlattice. Microst. 88(2015)501-507.
- [13] Diana Nesheva, Valeri Dzhurkov, Irina Stambolova, Vladimir Blaskov, Irina Bineva, Jose Maria Calderon Moreno, Silviu Preda, Mariuca Gartner, Temenuga Hristova-Vasileva, Maria Shipochka, Mater. Chem. Phys. 209(2018)165-171.
- [14] Seval Aksoy, Yasemin Caglar, Saliha Ilican, Mujdat Caglar, J. Alloys Compd. 512(2012)171-178.
- [15] Reza Ebrahimifard, Mohammad Reza Golobostanfard, Hossein Abdizadeh, Appl. Surf. Sci. 290(2014)252-259.
- [16] Solbaro Kim, Changheon Kim, Chaehwan Jeong, Sangwoo Lim, Curr. Appl. Phys. 14(2014)862-867.
- [17] Chanhyoung Park, Solbaro Kim, Changheon Kim, Chaehwan Jeong, Sangwoo Lim, Thin Solid Films 548(2013)263-269.
- [18] Jiao Yang, Yiling Jiang, Linjie Li, Meizhen Gao, Appl. Surf. Sci. 421 (2017)446-452.
- [19] Fenggui Wang, Xiaoru Zhao, Libing Duan, Yajun Wang, Hongru Niu, Amjed Ali, J. Alloys Compd. 623(2015)290-297.
- [20] Wenzuo Wei, Ruijin Hong, Jinxia Wang, Chunxian Tao, Dawei Zhang, J. Mater. Sci. Technol. 33(2017)1107-1112.
- [21] Yanli Li, Yong Mena, Xiangdong Kong, Zhaoshun Gao, Li Han, Xiaona Li, Appl. Surf. Sci. 428(2018)191-198.
- [22] Xiangdong Kong, Qian Dai, Li Han, Qingrong Feng, Zhaoshun Gao, Yanwei Ma, Mingzhang Chu, Hong Xue, Jianguo Li, Furen Wang, Yibing Zhang, Supercond. Sci. Tech. 24 (2011)105013.
- [23] S. Mridha, D. Basak, J. Phys. D 40(2007)6902-6907.
- [24] Meizhen Gao, Jing Liu, Huina Sun, Xiaonan Wu, Desheng Xue, J. Alloys Compd. 500(2010)181-184.
- [25] Mingwei Zhu, Hui Huang, Jun Gong, Chao Sun, Xin Jiang, J. Appl. Phys. 102 (2007)1-6.
- [26] Zhanchang Pan, Junming Luo, Xinlong Tian, Shoukun Wu, Chun Chen, Jianfeng Deng, Chumin Xiao, Guanghui Hu, Zhigang Wei, J. Alloys Compd. 583(2014)32-38.
- [27] Zi-Neng Ng, Kah-Yoong Chan, Thanaporn Tohsophon, Appl. Surf. Sci. 58(2012)9604-9609.
- [28] Fenggui Wang, Xiaoru Zhao, Libing Duan, Yajun Wang, Hongru Niu, Amjed Ali, J. Alloys Compd. 623(2015)290-297.
- [29] Akio Kuroyanagi, J. Appl. Phys. 66(1989)5492.
- [30] T V Vimalkumar, N Poornima, K B Jinesh, C Sudha Kartha, K P Vijayakumar, Appl. Surf. Sci. 257(2011)8334-8340.
- [31] L.-W. Lai, C.-T. Lee, Mater. Chem. Phys. 110(2008)393-396.
- [32] Sreetama Dutta, S Chattopadhyay, Manas Sutradhar, Anindya Sarkar, Mahuya Chakrabarti, D Sanyal, Debnarayan Jana, J. Phys-Condens. Mat. (2007)236218.
- [33] R Vinodkumar, K J Lethy, Panneerselvam Arunkumar, Renju R Krishnan, N Venugopalan Pillai, V P Mahadevan Pillai, Reji Philip, Mater. Chem. Phys. 121(2010)406-413.
- [34] G Li, X B Zhu, X W Tang, W H Song, Z R Yang, J M Dai, Y P Sun, X Pan, Sy Dai, J. Alloys Compd. 509(2011)4816-4823.
- [35] V. Srikant, D. R. Clarke, J. Appl. Phys. 81(1997)6357-6364.
- [36] I Hamberg, C G Granqvist, Karlfredrik Berggren, B E Sernelius, L Engstrom, Phys. Rev. B 30(1984)3240.Charles Kittel, Chemical Industry Press, Beijing, 2005