Effect of post-annealing on the structure and optical properties of ZnO films deposited on Si substrates

Hong Jun WANG, Yuan Yuan Zhu
Department of Physics, Shaanxi University of Science and Technology, Xi’an 710021, China
Email: zhuyuanyuan@sust.edu.cn

Abstract. Thin ZnO films were deposited on silicon (Si) substrates by radio frequency (RF) magnetron sputtering method at 300°C and the post-annealing for the as-deposited ZnO films was carried out at different temperatures of 500, 700 and 800°C respectively. The structure and optical properties of the ZnO films at different annealing temperatures were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and photoluminescence (PL), respectively. The XRD patterns show that all the ZnO films have a high preferred c-axis orientation, which is perpendicular to the Si substrates. The grain size increases as the increasing the annealing temperature, as indicated from both XRD patterns and AFM images. Besides that, the ZnO film at annealing temperature of 700°C shows the strongest UV emission intensity and the narrowest full width at half maximum (FWHM).

1. Introduction
Zinc oxide (ZnO), with a large exciton binding energy of 60 meV and a wide bandgap of 3.4 eV, has attracted considerable attentions due to its great potential applications in optical and electronics, such as photodetectors, gas sensors and piezoelectric sensors, etc. [1-4]. The crystal quality of ZnO films is a key aspect to realize its applications in industry. Especially, the effects of post annealing on the crystalline structure as well as the optical properties of ZnO films is quite important in realizing in potential applications [5, 6]. Therefore, there is a strong interest to understand the relation between the structure and optical properties of ZnO films with the annealing temperature.

Many methods have been employed to grow ZnO thin films, such as sol-gel process [7], spray pyrolysis [8], chemical vapor deposition [9] and radio frequency (RF) magnetron sputtering, etc. [10]. Among these methods, the RF magnetron sputtering technique is widely used in depositing ZnO films due to unique properties of the as-prepared films, for instances, its relative smooth surface and the growth orientation highly along c-axis [11].

In this present work, thin ZnO films were successfully grown on silicon (Si) substrates at 300°C by RF magnetron sputtering system. The as-deposited ZnO films were annealed at temperature of 500, 700 and 800°C in oxygen ambient for 0.5 h. The influence of the annealing temperature on the structure and optical properties of ZnO films at different annealing temperatures are systematically investigated.

2. Experiments
ZnO films were grown on p-type Si (100) substrates by RF magnetron sputtering system using the ceramic ZnO target. Before deposition, the substrates were ultrasonically cleaned in sequence in acetone, methanol and de-ionized water respectively. The chamber was evacuated to a base pressure of
5.0×10^{-9} \text{Torr}. During the sputtering process, the pressure and temperature were kept at 4.0×10^{-4} \text{Torr} and 300°C, respectively. Subsequently, the as-deposited ZnO films were annealed at temperature of 500, 700 and 800°C in oxygen ambient for 0.5 h. A slow cooling rate was maintained to avoid the possibility of inducing any stress and strain in the films.

The crystalline structure of the ZnO films was characterized by X-ray diffraction (XRD) with Cu Ka radiation. The surface topography was analyzed using the atomic force microscope (AFM) operating in tapping mode. Room temperature photoluminescence (PL) spectra were recorded by PerkinElmer luminescence spectrometer. All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the as-deposited ZnO film and the following annealed films in oxygen ambient at annealing temperature of 500, 700 and 800°C. All the ZnO films exhibit the strongest prominent (002) diffraction peak, indicating the preferential orientation with the c-axis perpendicular to the substrates. The small peak at 32.9° is caused by the (002) plane of the Si substrates [12]. Besides that, no other peaks corresponding to the ZnO films are observed in the measured region.

![XRD patterns of ZnO films grown on Si substrates annealed in oxygen ambient at different temperatures: (a) general scan and (b) magnified pattern of (002) diffraction peak.](image)

The intensity of (002) peak for ZnO films increases as increasing annealing temperature and it reaches the maximum value at annealing temperature of 700°C. It is known that, as increasing annealing temperature, the film atoms get high energy to enhance the mobility. Eventually, the defects in the films decrease and the quality of the films is enhanced. However, the intensity quickly decreases
for ZnO film at annealing temperature of 800℃, which can be seen from the magnified pattern in Fig. 1(b). This can be explained by the formation of porosity at ZnO/Si interface at annealing temperature of 800℃. As a result, the quality of the ZnO film is reduced. [13]. Besides that, the position of the (002) peak gradually increases from the standard powder value of 34.42° to a maximum 34.71° as increasing the annealing temperature, as shown in Table 1. This result indicates that the increase of the annealing temperature leads to the enhancement of the residual stress in the thin ZnO films [14].

The full width at half maximum (FWHM) values of (002) peak were 0.194°, 0.188°, 0.171° and 0.140° for ZnO films of the as-deposited, at annealing of 500℃, 700℃ and 800℃, respectively (Table 1). The value of FWHM decreases with increasing annealing temperature, which relates to the increase of the grain size. The average grain size can be calculated from the XRD patterns by Scherrer formula, which is defined as: D=0.9λ/(βcosθ), where λ, β and θ are the X-ray wavelength (0.154 nm), FWHM of the ZnO (002) peak and the diffraction angle, respectively.

The surface morphology of ZnO films at different annealing temperatures was measured by AFM, as shown in Fig. 2. It is noted that the grain size increases as increasing the annealing temperature, which is consistent with the calculation results from the XRD patterns. The similar observations also have been reported in other works [15, 16]. It indicates that the annealing treatment introduces a certain extent of redistribution as well as a slight growth of ZnO grains in the films. However, the grain size of ZnO films analyzed by AFM is much larger than that calculated from the XRD patterns, as shown in Table 1. This difference is probably due to that the grain size measured from AFM is the surface morphology of coalesced grains which presents the particle size [14].

| Sample                  | Peak Position (deg.) | FWHM (deg.) | Grain size (nm) XRD | Grain size (nm) AFM |
|-------------------------|----------------------|-------------|---------------------|---------------------|
| As-deposited (300℃)    | 34.429               | 0.194       | 50.2                | 54.38               |
| 500℃                   | 34.466               | 0.188       | 52.2                | 70.11               |
| 700℃                   | 34.642               | 0.171       | 60.1                | 107.70              |
| 800℃                   | 34.712               | 0.140       | 84.8                | 188.28              |
During the annealing process, small crystallites coalesce together to form larger crystallites as the annealing temperature increases up to 700°C. Eventually, the grain sizes increase as increasing the annealing temperature. This is corresponding to the increase of (002) peak intensity in XRD patterns as the increase of annealing temperature up to 700°C. However, the ZnO films become cracked at a higher annealing temperature of 800°C and an incoherent interface between ZnO films and silicon substrates occurs due to the large difference in thermal expansion coefficient [12]. This is also the main reason which is responsible for the decrease of (002) peak intensity at higher annealing temperature of 800°C.

The PL spectrum of ZnO film usually consists of UV emission band and visible broadband emission, which are corresponding to the exciton and structural defects related recombination, respectively. All the ZnO films in our work show so weakly visible broadband emission that they cannot be properly analyzed to the limitation of the used instrument. Fig. 3(a) illustrates the PL spectra measured in the range of 350 to 450 nm for the ZnO films at different annealing temperatures. The strong UV luminescence at around 380 nm is assigned to the near-band-edge (NBE) emission, which is observed for all the ZnO films.

As increasing the annealing temperature up to 700°C, the intensity of the UV emission is gradually improved (Fig. 3(a)) and the FWHM of the NBE emission decreases (Fig 3(b)). It indicates that the crystal quality is improved as increasing the annealing temperature, which is consistent with the XRD results. However, the reversed trend is observed for ZnO film at annealing temperature of 800°C. This is because that the ZnO film become cracked, which is also discussed in AFM images. The above results indicate that the quality of ZnO film improves as increasing the annealing temperature and reaches the best quality at the temperature of 700°C. Besides that, the film quality will decrease at a higher annealing temperature.

![Figure 2](image-url)
Figure 3 (a) Room temperature PL spectra and (b) FWHM of NBE emission peak at around 380 nm of ZnO thin films grown on Si substrates annealed at different temperature.

4. Conclusion
In summary, thin ZnO films were deposited on Si substrates by RF magnetron sputtering method. The structure and optical properties of ZnO films at different annealing temperatures were systematically investigated. XRD patterns demonstrated that the all the ZnO thin films showed a high preferred orientation with the c-axis perpendicular to the substrates. It was noted that the grain size increased as increasing the annealing temperature, calculating from both AFM images and XRD patterns. The ZnO film showed the strongest UV emission intensity at annealing temperature of 700°C. The results showed that the quality of the ZnO films can be improved by the annealing treatment and the best crystal quality of the film was obtained at annealing temperature of 700°C.

References
[1] Ye L H, Freeman A J, Delley B, Half-metallic ferromagnetism in Cu-doped ZnO: Density functional calculations[J]. Physical Review B, 2015, 73: 73.
[2] Sagalowicz L, Fox G R, Planar defects in ZnO thin films deposited on optical fibers and flat substrates[J]. Journal of Materials Research, 2017, 14(5): 1876-1885.
[3] Noori K, Giustino F, Ideal energy-level alignment at the ZnO/P3HT photovoltaic interface[J]. Advanced Functional Materials, 2015, 22(24): 5089-5095.
[4] Riaz M, Song J, Nur O, Wang Z L, Willander M, Study of the piezoelectric power generation of ZnO nanowire arrays grown by different methods[J]. Advanced Functional Materials, 2015, 21(4): 628-633.
[5] Wei X Q, Zhang Z G, Liu M, Chen C S, Sun G, Xue C S, Zhuang H Z, Man B Y, Annealing effect on the microstructure and photoluminescence of ZnO thin films[J]. Materials Chemistry &
Physics, 2007, 101(2): 285-290.

[6] Wei S F, Lian J S, Wua H, Annealing effect on the photoluminescence properties of ZnO nanorod array prepared by a PLD-assistant wet chemical method[J]. Materials Characterization, 2010, 61(11): 1239-1244.

[7] Moszak K, Szczurek A, Babiarczuk B, Borak B, Krzak J, ZnO sol-gel oxide coatings as materials for UV optical filters[J]. Advanced Materials Letters, 2017, 8(4): 542-545.

[8] Kulandaisamy A J, Reddy J R, Srinivasan P, Babu K J, Mani G K, Shankar P, BalaguruRayappan J B B, Room temperature ammonia sensing properties of ZnO thin films grown by spray pyrolysis: Effect of Mg doping[J]. Journal of Alloys & Compounds, 2016, 688: 422-429.

[9] Feng Q J, Liang H W, Mei Y Y, Liu J Y, Ling C C, Tao P C, Pan D Z, Yang Y Q, ZnO single microwire homojunction light emitting diode grown by electric field assisted chemical vapor deposition[J]. Journal of Materials Chemistry C, 2015, 3(18): 4678-4682.

[10] Oh M S, Navamathavan R, Hydrogen incorporation effect in phosphorus-doped p-type ZnO thin films grown by radio-frequency magnetron sputtering[J]. Rsc Advances, 2017, 7: 16119-16125.

[11] Gonçalves R S, Barrozo P, Cunha F, Optical and structural properties of ZnO thin films grown by magnetron sputtering: Effect of the radio frequency power[J]. Thin Solid Films, 2016, 616: 265-269.

[12] Phan D T, Chung G S, The effect of post-annealing on surface acoustic wave devices based on ZnO thin films prepared by magnetron sputtering[J]. Applied Surface Science, 2001, 257(9): 4339-4343.

[13] Fang Z B, Yan Z J, Tan Y S, Liu X Q, Wang Y Y, Influence of post-annealing treatment on the structure properties of ZnO films[J]. Applied Surface Science, 2005, 241(3-4): 303-308.

[14] Chu S Y, Water W, Liaw J T, Influence of postdeposition annealing on the properties of ZnO films prepared by RF magnetron sputtering[J]. Journal of the European Ceramic Society, 2003, 23(10): 1593-1598.

[15] Lin L Y, Kim D E, Effect of annealing temperature on the tribological behavior of ZnO films prepared by sol–gel method[J]. Thin Solid Films, 2009, 517(5): 1690-1700.

[16] Kim H W, Kim N H, Annealing effect for structural morphology of ZnO film on SiO2 substrates[J]. Materials Science in Semiconductor Processing, 2004, 7(1-2): 1-6.