Vacuum 84 (2010) 1280–1286

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Low temperature annealing effects on the structure and optical properties of ZnO films grown by pulsed laser deposition

B.L. Zhu [a,*], X.Z. Zhao [b], F.H. Su [c], G.H. Li [c], X.G. Wu [c], J. Wu [a], R. Wu [a]

[a] Department of Metal Materials Engineering, School of Materials and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, People's Republic of China
[b] Department of Physics, Wuhan University, Wuhan 430072, People's Republic of China
[c] National Laboratory for Superlattices and Microstructures Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, People's Republic of China

ARTICLE INFO

Article history:
Received 16 October 2009
Received in revised form
29 January 2010
Accepted 31 January 2010

Keywords:
ZnO
Pulsed laser deposition (PLD)
Annealing treatment
Photoluminescence (PL)

ABSTRACT

ZnO thin films were deposited on glass substrates at room temperature (RT) ~500 °C by pulsed laser deposition (PLD) technique and then were annealed at 150–450 °C in air. The effects of annealing temperature on the microstructure and optical properties of the thin films deposited at each substrate temperature were investigated by XRD, SEM, transmittance spectra, and photoluminescence (PL). The results showed that the c-axis orientation of ZnO thin films was not destroyed by annealing treatments; the grain size increased and stress relaxed for the films deposited at 200–500 °C, and thin films densified for the films deposited at RT with increasing annealing temperature. The transmittance spectra indicated that E_g of thin films showed a decreased trend with annealing temperature. From the PL measurements, there was a general trend, that is UV emission enhanced with lower annealing temperature and disappeared at higher annealing temperature for the films deposited at 200–500 °C; no UV emission was observed for the films deposited at RT regardless of annealing treatment. Improvement of grain size and stoichiometric ratio with annealing temperature can be attributed to the enhancement of UV emission, but the adsorbed oxygen species on the surface and grain boundary of films are thought to contribute the annihilation of UV emission. It seems that annealing at lower temperature in air is an effective method to improve the UV emission for thin films deposited on glass substrate at substrate temperature above RT.

1. Introduction

ZnO exhibits great potential in many fields, including surface acoustic wave (SAW) filters, transparent electrodes in solar cells, ultraviolet light emitting devices, and gas sensors due to its attracting electrical and optical properties [1–4]. Various techniques such as radio-frequency (RF) magnetron sputtering, sol-gel, metalorganic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), and pulsed laser deposition (PLD) had been developed to prepare ZnO thin films. Among those techniques, the PLD method seems to be the most attractive since it can offer the potential of growing high quality thin films at relatively lower substrate temperature than other techniques. The properties of ZnO films prepared by PLD method depend on the following process variables: substrate temperature, target-to-substrate distance, condition in chamber (e.g. O_2 pressure), and laser parameters such as power density, wavelength, deposition time, and pulse repetition rate [5–16].

Among the process parameters of PLD technique, substrate temperature directly affects mobility rate, re-evaporation, and crystallization of deposited species on the substrate surface, and thus affects the microstructure and properties of thin films. After the thin films are prepared under a certain condition, crystallinity and stoichiometric ratio of the thin films can be further modified by annealing treatment. Some researchers have study the effects of substrate temperature and post-annealing treatment on microstructure and properties of ZnO films grown by PLD. In these reports, most ZnO films were deposited on crystal substrates at substrate temperature from RT to above 500 °C [7–16], and post-annealing temperature is usually higher than 400 °C and higher than that of substrate temperature while deposition [17–22]. It is found that 400–600 °C high temperature is necessary for relieving accumulated strain energy, diminishing defects, and enlarging grain size to get strong UV emission. However, it is also found that aging (i.e. thin films are under RT and air atmosphere for a long time) also affects the properties of ZnO thin films [17,23–25]. This also indicates that microstructure and properties of ZnO films can be adjusted by lower temperature annealing for a relatively long time. For some substrate materials, such as glass and polymer, they cannot be subjected a higher temperature, thus low temperature

* Corresponding author. Tel.: +86 27 68862305.
E-mail address: zhubailin97@hotmail.com (B.L. Zhu).

0042-207X/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2010.01.059

annealing may be a main approach to further improve the properties of thin films. However, few report was focus on low temperature annealing effects on the structure and optical properties of ZnO films grown by PLD.

In this paper, ZnO thin films were prepared by PLD at different substrate temperatures, and the influences of the low temperature annealing on the microstructure, transmittance properties, and photoluminescence (PL) characteristic of ZnO films had been studied.

2. Experimental procedures

ZnO thin films were deposited on glass substrates in a PLD system. The target was sintered ZnO ceramic disk (99.99% purity) with 2.5 cm in diameter and 0.5 cm in thickness. Glass sheets, which were used as the substrate for ZnO films deposition, were cleaned in an ultrasonic bath with acetone for 10 min before being loaded into the chamber. The substrates were placed parallel to the target surface with a 7 cm distance. A pulsed excimer laser (KrF; $\lambda = 248$ nm, COMPex205, Lambda Physik) was used and operated at pulsed width of 25 ns and repetition rate of 5 Hz. The laser beam was focused through a 50 cm focal lens onto a rotating target at a 45° angle of incidence. The laser energy was fixed at 348 mJ/pulse, yielding an energy density at target surface of approximately 2.78 J/cm^2. The deposition chamber was initially evacuated to 3×10^{-3} Pa, then oxygen was introduced into the chamber to maintain 12 Pa. The substrate temperature was varied from room temperature (RT) to 500 °C, measured using a thermocouple and was controlled by a feed back controlled heater. For all the substrate temperature, a deposition time of 10 min was maintained. The prepared ZnO films at different substrate temperatures were subjected to annealing treatment in air for 2 h at temperature of 150, 300, and 450 °C, respectively.

An X-ray diffraction apparatus (XRD, BDX3200, Perking University, China) with Cu $K_{\alpha 1}$ incident radiation was carried out to identify the phase structure of the films. The surface morphology of the films was studied using a field emission scanning electron microscope (FE-SEM, Sirion, FEI). The film thickness was measured by a nano-step instrument (Form Talysurf S4C, Taylor Hobson). The thickness of films was about 150–200 nm. The optical transmittance properties of ZnO films were measured by using a UV-visible-near IR spectrometer (Cary 5000, Varian). The photoluminescence (PL) measurements were performed using a He–Cd laser with an excitation wavelength of 325 nm.

3. Experimental results and discussion

The XRD patterns of ZnO thin films deposited at different substrate temperatures have been shown in our published paper [7], and typical XRD patterns of ZnO films annealed at different temperatures are shown in Fig. 1. It is found that XRD patterns of ZnO thin films deposited at different temperatures and annealed at different temperatures show the same form, that is only a (002) diffraction peak is detected in the films. This indicates that ZnO films prepared by PLD show a good c-axis orientation perpendicular to the substrate and also means that orientation of prepared ZnO films is not destroyed after further annealing treatment. The diffraction peak angles for ZnO films deposited at different temperatures as a function of annealing temperature are shown in Fig. 2. As seen in Fig. 2, diffraction peak angle of the films prepared at RT, 200, 350 and 500 °C appears at 34.33, 34.51, 34.54, and 34.56°, respectively. Compared with the (002) peak position of ZnO powder ($2\theta = 34.42°$), the diffraction angle of the films grown at RT decreases, which results in the increase of *c*-axis value. This indicates that ZnO films grown at RT suffer compressive stress along the interfaces [5,26]. The diffraction angle of the films grown at 200–500 °C increases in comparison with bulk ZnO, which indicates that *c*-axis values of ZnO films are shorted. So the stress in ZnO film shows tensile along the interfaces. The stress is related to the defects in the films, i.e., the compressive stress may be due to zinc interstitials, but the tensile stress may be due to the oxygen vacancies in the lattice of ZnO crystallites in the film. In addition to intrinsic stress originating from the defects (zinc interstitials or oxygen vacancies) in the ZnO lattice, the stress also originates from thermal stress, which results from the difference in coefficient of thermal expansion (CTE) of ZnO thin films and glass substrate [7,26]. Since CTE of ZnO along *a*-axis is lower than that of glass substrate, the compressive stress will be generated in the films when substrate temperature drops from high temperature down to RT. When ZnO thin films are deposited at RT, no thermal stress exists in the thin films, and zinc interstitials result in the compressive stress in the thin films. When the thin films are deposited at 200–500 °C, both intrinsic and thermal stress exist in the thin films, but finally tensile stress resulting from oxygen vacancies is dominative in the films.

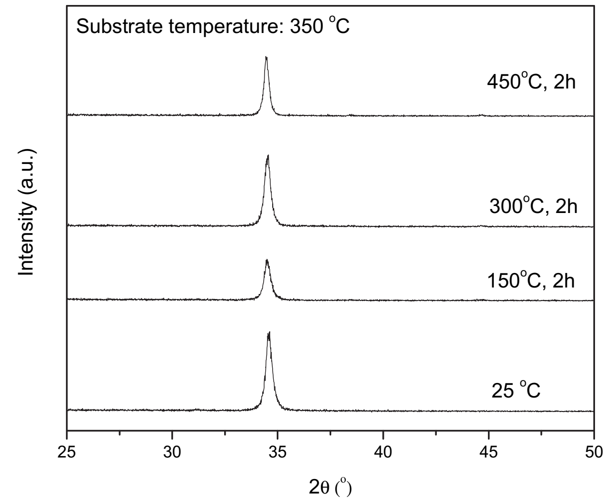

Fig. 1. Typical XRD pattern of ZnO films annealed at different temperatures.

For the ZnO thin films deposited at RT, it is observed that diffraction peak angle is still lower than that of bulk ZnO after annealing at different temperatures. For the ZnO thin films deposited at 200–500 °C, diffraction peak angle shows decreased trend with increasing annealing temperature. Obviously, the defects in the films are modified by annealing treatment, and the type and

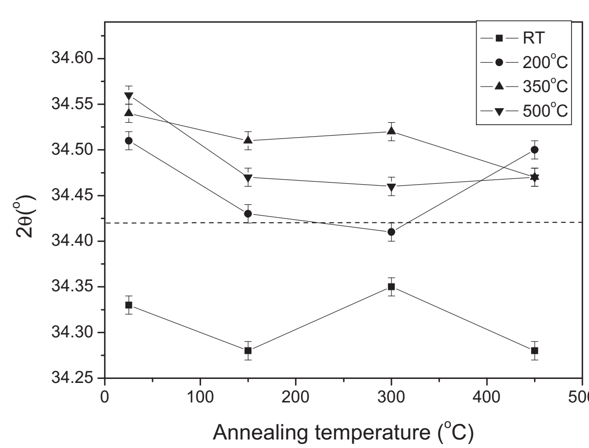

Fig. 2. The position of (002) diffraction peak for the ZnO films deposited at different substrate temperatures as a function of annealing temperature.