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Effect of high-temperature annealing on the structural and optical properties of ZnO films

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Abstract

The annealing effect on the optical properties of ZnO epilayers was reported. The ZnO thin films were grown using metal organic chemical vapor deposition method, and annealed in atmosphere at 850 °C for different time periods. Double-crystal X-ray diffraction showed that, after annealing, the density of the edge-dislocations decreased dramatically upon annealing, however, the screw-dislocations were not affected significantly. Strong green photoluminescence was observed in the annealed ZnO films while the as-grown films showed only near band edge emission. The deterioration of the optical properties in the annealed film, however, only occurred near the film surface in a very thin layer.

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Keywords: Zinc oxide; Annealing; Optical properties; X-ray diffraction

1. Introduction

ZnO is well-known as ceramic and phosphor material for decades. The discovery of room temperature ultraviolet (UV) lasing action in 1998 [1,2] triggered worldwide interests in research of ZnO as a promising UV semiconductor laser material to compete with GaN. ZnO has a large exciton binding energy (60 meV) [3], in addition, its band gap energy can be extended to 4.0 eV by adding Mg and narrowed to 2.8 eV by alloying with CdO [4], implying its high potential for use in many applications especially for light emitting devices. Using molecular beam epitaxy, metalorganic chemical vapor deposition (MOCVD), pulse laser deposition and other methods, high quality ZnO layers have been grown and their structural and optical properties have been extensively studied [5–7].

Thermal annealing is a widely used method to improve crystal quality and to study structural defects in materials. For semiconductors, thermal annealing is also used to activate dopants and to alloy ohmic contacts. During an annealing process, dislocations and other structural defects will move in the material and adsorption/decomposition will occur on the surface, thus the structure and the stoichiometric ratio of the material will change. The structural and optical properties are vital for semiconductor devices especially for light emitting devices. It is necessary to study how these properties are affected by thermal annealing. For ZnO films, several researches on thermal annealing have been reported [8–10]. In those researches, X-ray diffraction (XRD) symmetric (002) ω-scan or ω-2θ scan and photoluminescence (PL) spectroscopy were used to characterize the structural and optical properties of the ZnO samples. It is well known that (002) rocking curves cannot completely reflect the structural quality of ZnO films because it is insensitive to edge dislocations [11]. On the other hand, PL measurement can only provide information from a thin surface layer rather than the whole film due to the large

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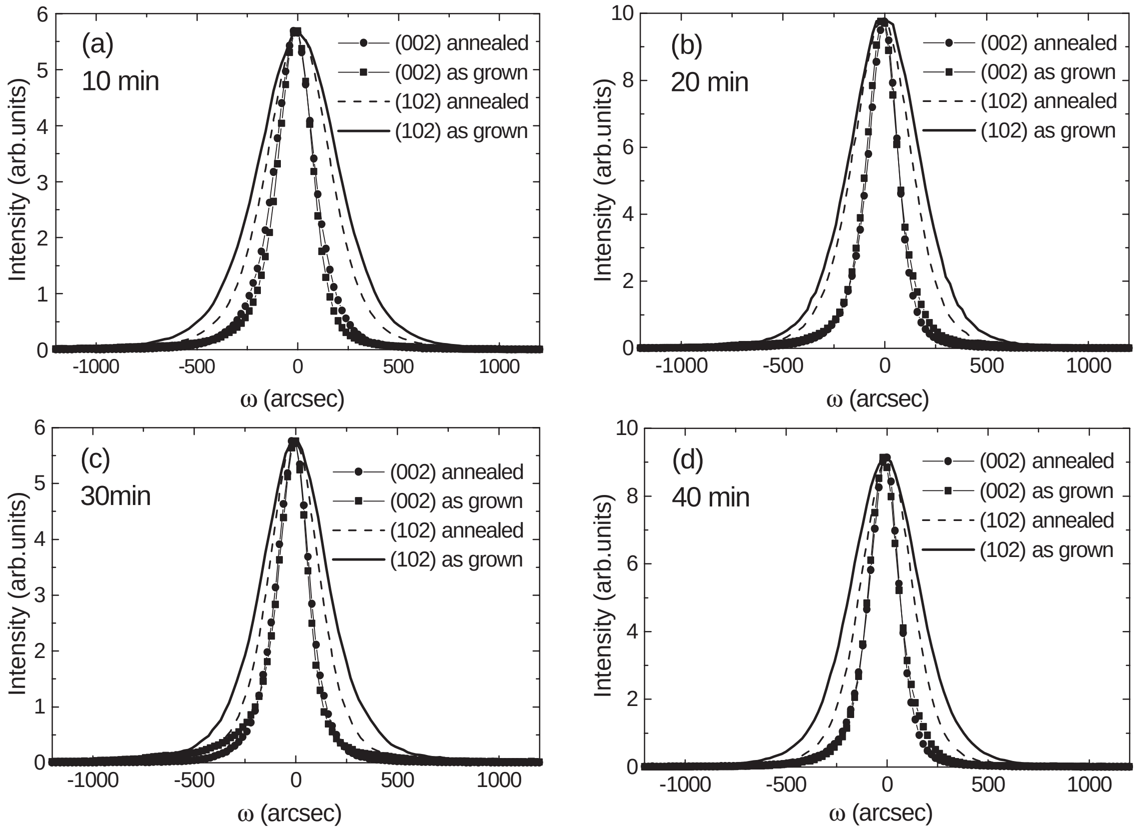

Fig. 1. (002) and (102) rocking curves of the ZnO samples measured before and after annealing. (a) 850 °C annealing for 10 min. (b) 850 °C annealing for 20 min. (c) 850 °C annealing for 30 min. (d) 850 °C annealing for 40 min. All the curves were normalized for plotting purpose.

absorption coefficient of the material for the excitation laser. To understand the effect of thermal annealing on the film properties more precisely, XRD asymmetric scan in skew geometry and etching process are needed. In the present paper we made an attempt to deal with these problems.

2. Experimental details

ZnO films were grown using a homemade vertical atmospheric pressure MOCVD system. Al_2O_3 (001) wafers were used as the substrates. Diethyl zinc and H_2O were used as the Zn and O precursors. The film thickness was about 3.0 μm. Four pieces from a 2-inch ZnO wafer were annealed at temperature 850 °C in atmosphere using a quartz-tube furnace for 10, 20, 30, and 40 min, respectively. Rocking curves of all as-grown as well as the annealed samples were measured using a double-crystal X-ray diffractometer (QC200, BEDE Instruments, UK). Cu Kα_1 line was used as the source and Ge (004) was used as the reference crystal. The full width at half maxium (FWHM) values of the rocking curves were obtained by Pseudo-Voigt fitting. Room temperature photoluminescence spectra of the samples were measured before and after annealing using 325 nm line of a He–Cd laser (10 mW) as the excitation source (WDP500-D, Beijing Rayleigh Analytical Instrument Corp.). After annealing, the four samples were etched for 5 min by an induction-coupled plasma (ICP) etching system (2B, Beijing Chuangweina Tech. Co., Ltd.) and then room temperature PL spectra of the films were measured again. The plasma source used for etching was mixture of freon and argon. To measure the etching depth, a reference sample

Table 1
(002) and (102) FWHM values of ZnO samples measured before and after 850 °C annealing for various time

Diffraction plane	Treatment	FWHM (arc sec)			
		10-min-anneal sample	20-min-anneal sample	30-min-anneal sample	40-min-anneal sample
(002)	As grown	202	181	171	179
(002)	Annealed	229	176	196	175
(102)	As grown	447	400	387	399
(102)	Annealed	376	337	291	300