Vacuum 84 (2010) 1315–1318

Contents lists available at ScienceDirect

Vacuum

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

Study on Raman line at 1080.2 cm^{-1} in ZnO thin films prepared under high RF power

Qiong Xu, Xingwen Zhu*, Fang Zhang, Longxing Yang, Wenzhong Jiang, Xiao Zhou

School of Materials Science and Engineering, Shanghai University, Shanghai 200072, PR China

ARTICLE INFO

Article history:
Received 11 November 2009
Received in revised form
9 February 2010
Accepted 16 February 2010

Keywords:
Raman scattering
Photoluminescence
RF magnetron sputtering
Zinc thin film

ABSTRACT

ZnO thin films were prepared on glass or on homo-buffer/glass by a RF magnetron sputtering method at RF power of 100–550 W. The structural and Raman characteristics of the films were analyzed by X-ray diffraction and Raman scattering. There appeared a sharp peak of 1080.2 cm^{-1} near the A_1(2LO) mode (1156 cm^{-1}) of ZnO in the Raman spectra when the RF power was higher than 300 W. In this case, the (100) peak of ZnO film appeared obviously. It was speculated that the Raman mode at 1080.2 cm^{-1} was induced by the ordered distribution of Zn_i defects in ZnO lattice.

1. Introduction

ZnO is a direct band-gap material with a band gap at ~3.4 eV and a relatively deep excitonic binding energy of ~60 meV at room temperature [1], which makes it an excellent candidate for the fabrication of photonic devices. Recently, many efforts have been done on the preparation of ZnO thin films by various techniques such as metal organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), molecular beam epitaxy (MBE) and radio frequency (RF) magnetron sputtering. However, the films quality is considerably influenced by the unavoidable defects existed in ZnO lattice. Some reports focused the interest on analyzing the types and concentration, as well as the distribution of the defects in ZnO films [2–4]. Photoluminescent (PL) spectra is often used to detect the kinds of defects because the defects level inside the band gap is usually an emitting center which is easily observed in the PL spectra. Raman scattering is another useful method to gain insight into microscopic structural effects of materials, which can give information about the crystal structure on the scale of a few lattice constants. Any distortion of the lattice, excursion of the component, crystal defect, as well as phase transformation can be shown in Raman band [5,6].

In this work, we prepare ZnO thin films on glass by a RF magnetron sputtering method under different RF power, and use X-ray diffraction (XRD) and Raman spectroscopy to examine the influence of RF power on the structural properties of the samples.

2. Experimental

ZnO thin films were prepared by RF magnetron sputtering on lime-glass substrate and on low-power (LP) ZnO buffer/glass substrate, respectively. A disc of ZnO ceramics doped with 10 at% Li_2CO_3 with 120 mm in diameter was used as a target. The background pressure of the vacuum chamber was low than 3.0×10^{-4} Pa, and then high purity of argon (purity > 99.999%) was introduced to the chamber by a leak valve. The sputtering pressure was maintained at 0.3 Pa. The sputtering power was 100, 200, 300, 400, 500 and 550 W, respectively, and sputtering time was 120 min. The as-deposited samples were then annealed at 610 °C in air for 70 min. The low-power-deposited ZnO buffer layer (LP-buffer) was prepared on glass under 30 W RF power for 30 min and preheated at 610 °C before depositing the upper-layered films. The details about the preparation of LP-buffer are described in our previous paper [7].

The crystal structure of the samples was investigated by X-ray diffractometer (XRD, D/MAXXIIIC) which uses CuKα radiation. Raman and PL spectra of the films were obtained by means of Horiba Jobin Yvon system HR800 UV. Raman spectra were excited with the 514.5 nm line of an Ar^+ laser at an incident power of 20 mW and obtained in the range 50–1500 cm^{-1}.

3. Results and discussion

Wurtzite-type ZnO belongs to the space group C_{6V}^4, which has eight sets of phonon modes: $2E_2$, $2A_1$, $2E_1$ and $2B_1$, according to the group theory [8]. Among them, the $2B_1$ modes are not Raman and

---

* Corresponding author. .
E-mail address: xingwenzhu@shu.edu.cn (X. Zhu).

0042-207X/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2010.02.010

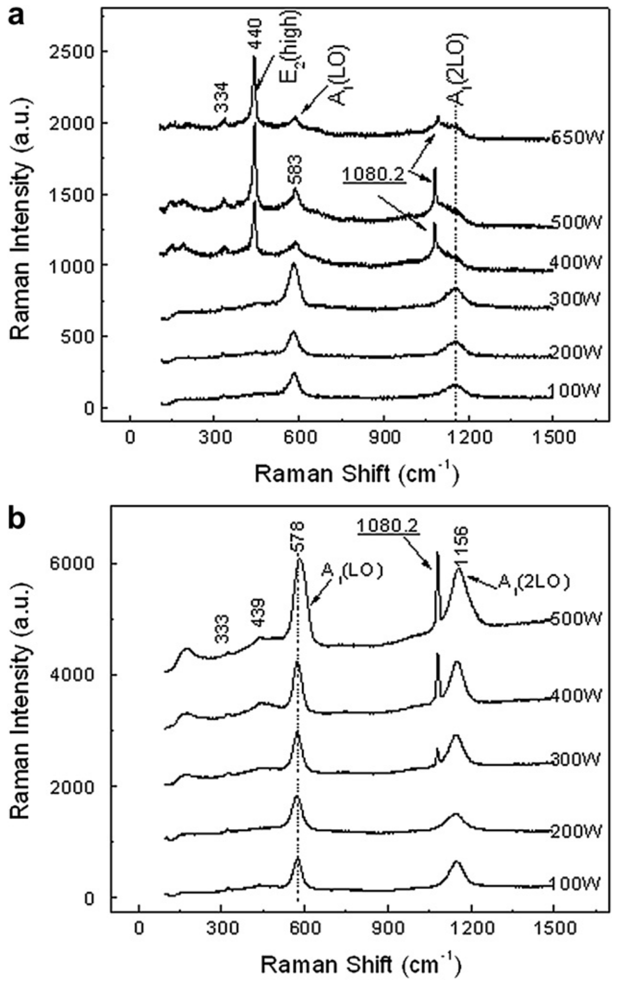

Fig. 1. Raman spectroscopy of ZnO films prepared under different RF power on (a): lime-glass substrate and (b): on LP-buffer/glass substrate.

infrared active (silent modes). Both A_1 and E_1 modes are polar and split into transverse (TO) and longitudinal optical (LO) phonons, all being Raman and infrared active. The two nonpolar E_2 modes are Raman active only.

Fig. 1 shows Raman spectra of the two groups ZnO films prepared under different RF power. The Raman lines around 334 cm^{-1}, 440 cm^{-1}, 578 cm^{-1} and 1156 cm^{-1} are observed for all the ZnO films, although some peaks cannot be distinguished obviously due to their weak Raman intensity. The lines around 440 cm^{-1}, 578 cm^{-1} and 1156 cm^{-1} are assigned to ZnO E_2(high) phonon mode, A_1 longitudinal optical mode A_1(LO) and A_1(2LO), respectively. The line at 334 cm^{-1} is assigned to multi-phonon processes, and occurs in ZnO films as well [9]. For the films prepared directly on lime-glass substrate as show in Fig. 1(a), with the increase of RF power, the E_2(high) line dominates the Raman spectra, while the intensity of the A_1(LO) band decrease. Generally, the E_2(high) mode represents the band characteristic of wurtzite phase [10]. The stronger peak implies the more perfect grains of the films prepared at higher RF power. The shift from 437 to 440 cm^{-1} of E_2(high) mode is caused by the compress stress existed in the films. The A_1(LO) mode is caused by the defects of O-vacancy, Zn interstitial, or their complexes [11]. The decrease of the A_1(LO) intensity implies the decrease of the defects in the films, which is correspond to the strong E_2(high) mode as discussed above. When introducing a LP-buffer between the lime-glass and ZnO film, the E_2(high) mode becomes weak and the A_1(LO) mode dominates the spectra, as shown in Fig. 1(b). The intensity of A_1(LO) mode increases with the increase of sputtering power, suggesting that more defects exist in the films prepared under higher RF power.

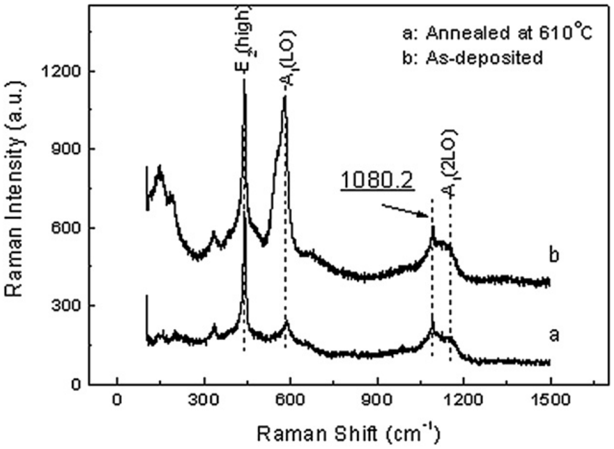

Fig. 2. Raman spectroscopy of annealed and as-deposited ZnO film prepared under 550 W.

There also exists an additional mode (AM) of Raman shift at 1080.2 cm^{-1} when the sputtering power is higher than 300 W for the ZnO films deposited directly on the lime-glass substrate, as shown in Fig. 1(a). It is observed that the appearance of

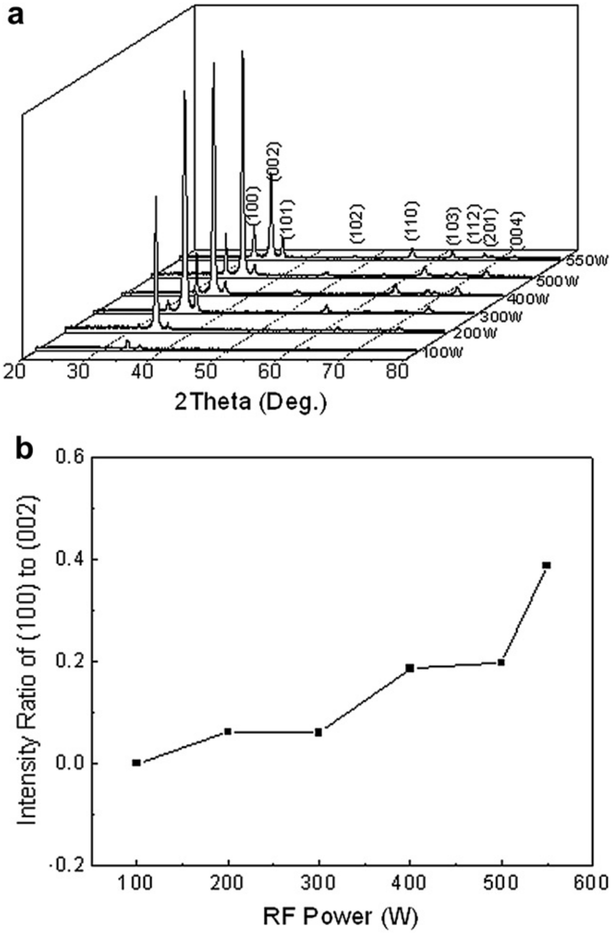

Fig. 3. (a): XRD patterns of ZnO films deposited on lime-glass substrate; (b) the intensity ratio of $I_{(100)}/I_{(002)}$ *vs.* deposited power.