Applied Surface Science 256 (2010) 2606–2610

Contents lists available at ScienceDirect

Applied Surface Science

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

Effects of annealing treatment on the formation of CO_2 in ZnO thin films grown by metal-organic chemical vapor deposition

Gaolin Zheng *, Anli Yang, Hongyuan Wei, Xianglin Liu **, Huaping Song, Yan Guo, Caihong Jia, Chunmei Jiao, Shaoyan Yang, Qinsheng Zhu, Zhanguo Wang

Key Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, People's Republic of China

ARTICLE INFO

Article history:
Received 17 September 2009
Received in revised form 29 October 2009
Accepted 31 October 2009
Available online 10 November 2009

Keywords:
ZnO
Metal-organic chemical vapor deposition
Infrared absorption
Surface

ABSTRACT

Post-growth annealing was carried out on ZnO thin films grown by metal-organic chemical vapor deposition (MOCVD). The grain size of ZnO thin film increases monotonically with annealing temperature. The ZnO thin films were preferential to *c*-axis oriented after annealing as confirmed by X-ray diffraction (XRD) measurements. Fourier transformation infrared transmission measurements showed that ZnO films grown at low temperature contains CO_2 molecules after post-growth annealing. A two-step reaction process has been proposed to explain the formation mechanism of CO_2, which indicates the possible chemical reaction processes during the metal-organic chemical vapor deposition of ZnO films.

1. Introduction

Since zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor with a large exciton binding energy of 60 meV, it has been considered as a promising candidate for short wave length light-emitting diodes, ultraviolet (UV) lasers, and transparent conducting materials [1–4]. The crystal quality is an important factor which obstructs the massive application of ZnO. Post-growth annealing has been proved to be an efficient approach to improve crystalline quality and optical properties of ZnO thin films [5–8]. On the other hand, for the control of growth modes to obtain high quality ZnO films, it is essentially required to elucidate the chemical vapor reaction processes during the growth. *In situ* monitoring by using Fourier transformation infrared (FT-IR) spectroscopy has been used to investigate the chemical species in the vapor phase during the metal-organic chemical vapor deposition (MOCVD) of ZnO using diethylzinc (DEZn) and nitrous oxide (N_2O) as source precursors, and possible chemical vapor reactions have been proposed [9]. Using infrared absorption spectroscopy, McCluskey and co-workers [10] have reported the presence of CO_2 molecules in ZnO nanoparticles which are synthesized by solution method. To our best knowledge, to date there is no report on CO_2 molecules in ZnO films grown by MOCVD.

In this work, post-growth annealing was performed on ZnO thin films grown by MOCVD at low temperature. *Ex situ* FT-IR measurements were performed to investigate the impurities in as-grown and annealed ZnO thin films. The chemical reaction processes during MOCVD growth of ZnO films are still not completely understood now. Study on the formation mechanism of impurities will be beneficial to understanding the processes of those reactions. It will also contribute to the control of growth processes to improve the crystal quality of ZnO films.

2. Experimental details

ZnO films were deposited on *c*-plane sapphire substrates using a home-made vertical low-pressure (76 Torr) MOCVD system. Bubbled diethylzinc (DEZn) and oxygen were used as the source of Zn and O, respectively. The flow rates of DEZn and oxygen gas were set at 48 scc/m (standard cubic centimeter per minute) and 1 sl/m (standard liter per minute), respectively. The DEZn was contained in stainless-steel bubble which was maintained at 18 °C and the pressure was kept at 800 Torr. Nitrogen was used as the carrier gas for both DEZn and oxygen. In order to reduce pre-reaction, DEZn and oxygen were introduced into the chamber separately by two nozzles. The growth temperature and time was 400 °C and 30 min, respectively. The rapid thermal annealing (RTA) was performed in the ambient of nitrogen at 600 °C, 700 °C, 800 °C, and 900 °C, respectively. The heating rate was 25 °C/s and the annealing time

* Corresponding author. Tel.: +86 10 82304968; fax: +86 10 82304968.
** Corresponding author at: No. 35, Tsinghua East Road, Haidian District, Beijing, China 100083, People's Republic of China.
E-mail addresses: zhenggl@semi.ac.cn (G. Zheng), xlliu@semi.ac.cn (X. Liu).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.10.109

was 120 s. Long time (30 min and 2 h) annealing was taken in a tube furnace under the protection of nitrogen.

The surface morphologies of the films were observed by field-emission scanning electron microscopy (FE-SEM: Hitachi-S480). The crystal structures of the films were characterized by XRD (Cu Kα, λ = 1.5406 Å). Room temperature infrared transmission spectroscopy was obtained by a IFS-120 HR Fourier transformation infrared spectrometer with a glow-bar light source and a liquid nitrogen cooled HgCdTe detector. The instrumental resolution was set at 16 cm^{-1}, and the spectra were averaged over 100 scans. Before performing the IR absorption measurement, the sample chamber was evacuated to about 30 Pa to avoid the gas phase contribution. X-ray photoelectron spectroscopy (XPS) measurements were carried out to identify the chemical states of C, O, Zn and their atomic concentrations by using a PHI Quantera SXM instrument with Al Kα (energy of 1486.6 eV) as the X-ray radiation source. To avoid the surface contamination effect, all the samples were subjected to a surface cleaning procedure by Ar^+ bombardment in the vaccum chamber of the XPS instrument and reduced a thickness of ~6 nm calculated by the sputtering rate.

3. Results and discussion

The crystal structures of the films were investigated by using θ–2θ scans of XRD as shown in Fig. 1. The as-grown ZnO film has three peaks at 34.64°, 32.17° and 36.49°, which indicate the orientations of (0 0 0 2), (1 0 $\bar{1}$ 0) and (1 0 $\bar{1}$ 1), respectively. After rapid thermal annealing, the peak of (0 0 0 2) enhanced, the intensities of (1 0 $\bar{1}$ 0) and (1 0 $\bar{1}$ 1) peaks decreased. This indicates that rapid thermal annealing can promote the *c*-axis orientation. The crystallite size may be estimated from the FWHM of the (0 0 0 2) diffraction peak by the Sherrer's equation [5]:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

where λ (0.15406 nm) is the wavelength of the X-ray and β is the FWHM in radians.

The calculated results were summarized in Table 1. From the table, we can conclude that RTA treatment can remarkably enlarge the grain size, especially annealing in higher temperature. The grain size increases with increasing annealing temperature can be explained by the coarsening and coalescence mechanism during processing of polycrystalline films [11]. For wurtzite ZnO, the *c*-plane (0 0 0 2) is a polar surface, and has large surface energy. The planes (1 0 $\bar{1}$ 0), (2 1 $\bar{1}$ 0), and (1 0 $\bar{1}$ 1) are non-polar or semi-polar

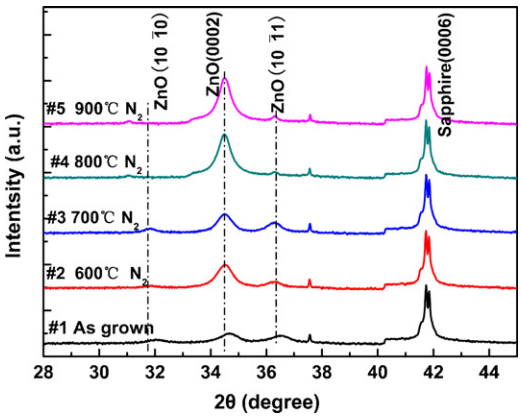

Fig. 1. XRD θ–2θ scans of samples as-grown and annealed in nitrogen for 2 min. (For interpretation of the references to color in this artwork, the reader is referred to the web version of the article.)

Table 1
The FWHM values of (0 0 0 2) peak and estimated grain size of as-grown and annealed ZnO films from XRD.

Samples	FWHM (°) of (0 0 0 2) peak	Grain size (nm) estimated from XRD
As-grown	0.55	16
600 °C, N_2	0.32	27
700 °C, N_2	0.33	26
800 °C, N_2	0.22	40
900 °C, N_2	0.11	77

planes with lower surface energy compared to the polar plane (0 0 0 2) [12]. Under thermodynamic equilibrium condition, the facet with higher surface energy is usually small in area, while the lower energy facets are larger. Thus, in epitaxial ZnO thin films, the *c*-axis oriented columnar grains is preferential, and the large side facets are usually (1 0 $\bar{1}$ 0) and (2 1 $\bar{1}$ 0), especially during high temperature annealing process. This consists with our XRD results.

Fig. 2 shows the SEM images of the surface morphology of the (a) as-grown and (b–e) annealed films. As shown in Fig. 2, the as-grown film has a triangular surface morphology, and the surface fluctuation is visible, which may be an indication of different orientations coexisted in the film. After annealing in nitrogen, the surface of the sample becomes flat, and the polygonal grains appear, with clearer grain boundaries. It can also be seen that the grain size increases with increasing annealing temperature, which is consistent with the XRD results. After annealing, hollows among grain boundaries appear. Cross-sectional SEM images show that the thicknesses of the samples are about 300 nm.

Room temperature infrared transmission spectra were shown in Fig. 3. A strong infrared absorption peak at the frequency of 2341 cm^{-1} was observed for samples annealed in nitrogen for 2 min. The sample annealed at 700 °C has the largest intensity of absorption at the frequency of 2341 cm^{-1}among all samples. This peak is assigned to asymmetric stretching vibration (ν3) of CO_2 molecule [10]. For a linear free CO_2 molecule, the ν3 vibrational frequency is estimated by

$$\nu = \kappa\sqrt{\frac{2}{M_C} + \frac{1}{M_O}} \quad (2)$$

where M_C and M_O are the masses of carbon and oxygen atoms, respectively; and κ is an effective spring constant. In our research, we only found the absorption peak of $^{12}CO_2$, and the absorption peak for $^{13}CO_2$ (2277 cm^{-1}) [10] did not appear. For comparison, we measured the FT-IR spectroscopy of samples grown at 600 °C or above, we found that they did not have the infrared absorption at 2341 cm^{-1}, nor after annealing. For samples grown at low temperature (lower than 500 °C), they did not show the infrared absorptions at 2341 cm^{-1}, but after annealing they all showed the infrared absorptions at 2341 cm^{-1}. We also took long time annealing (30 min and 2 h) at 800 °C in nitrogen gas for the samples grown at low temperature, we still found the absorption peaks at 2341 cm^{-1}, though the absorption peaks became much weaker as shown in Fig. 4. These phenomena seem a little strange, and making clear the reason of formation of CO_2 molecules during annealing process will be helpful to better understanding for the reaction processes of the MOCVD growth of ZnO. Before IR measurement was taken, the sample chamber was evacuated to about 30 Pa, the contribution from the CO_2 molecules from the gas phase was excluded. We also perform the IR measurement on the sapphire substrate at the same condition, it did not show any IR absorption at 2341 cm^{-1}. So the CO_2 must be from the sample itself.

According to Maejima and Fujita's research [9], the formation of CO_2 can be explained by a two-step reaction process. Firstly,