



Annealing and partial pressure ratio effects on ZnO films grown by metal-organic chemical vapor deposition using tert-butanol as oxidant

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ARTICLE INFO

Article history:

Received 30 June 2009

Received in revised form 20 June 2010

Accepted 8 July 2010

Available online 14 July 2010

Keywords:

Zinc oxide

Metal-organic chemical vapor deposition

Tert-butanol

Annealing

Raman scattering

Photoluminescence

ABSTRACT

ZnO films were deposited by metal-organic chemical vapor deposition on (0001) sapphire substrates at various partial pressure ratios of oxygen and zinc precursors ($R_{V/II}$). The annealing and the $R_{V/II}$ ratio effects on the vibrational and optical properties of ZnO films have been investigated by Micro-Raman scattering and low temperature photoluminescence (PL) spectroscopy. As confirmed by characterizations used in this study, the quality of the ZnO films was improved by thermal annealing at 900 °C in oxygen ambient. Raman spectra of the as-deposited films show a broad band (BB) centered at about 518 cm^{-1} whose intensity increases when the $R_{V/II}$ ratio decreases. After annealing, the intensity ratio of the BB to the E_2^H peak decreases rapidly with increasing the annealing time (t_{an}). The vibrational properties of the annealed films grown at $R_{V/II} = 1$ need only 1 h to be improved in contrast to those of films grown in Zn-rich condition, which need 4 h. From the E_2^H mode frequency, the residual stress in both the as-grown and the annealed films has been estimated. Micro-Raman measurements show that as-grown films are under a compressive stress which vanishes upon annealing and is not strongly dependent on t_{an} for t_{an} up to 1 h. PL spectra show that sharp donor bound exciton and A-free exciton emissions are observed for the as-deposited films grown at $R_{V/II} \geq 0.5$ and are enhanced after annealing for 1 h. However, in ZnO films grown in Zn-rich condition these emissions are absent and a $t_{\text{an}} = 4$ h is needed to annihilate non-radiative recombination centers and improve their luminescent efficiency.

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1. Introduction

ZnO is a direct, wide band gap semiconductor material with a large exciton binding energy (~60 meV). Its low price compared to other materials makes it a good candidate for industrial applications [1]. It has many interesting applications in optic-electronic devices, especially in the short wavelength region. Many growth techniques such as metal-organic chemical vapor deposition (MOCVD) [2,3], sputtering [4], pulsed-laser deposition [5] and molecular beam epitaxy [6] have been employed in order to obtain high quality ZnO films. The key factor to assure the high performance of semiconductor devices is high quality crystals. However, various defects often exist in ZnO semiconductors and affect their electronic and optical properties, such as oxygen vacancies (V_O), Zn interstitials (Zn_i), oxygen interstitials (O_i), Zn vacancies (V_{Zn}) and antisite oxygen (O_{Zn}) [7]. Some defects reduce both the device lifetime and the UV emission efficiency. To improve the luminescent efficiency, the density of non-radiative recombination centers in materials should be as low as possible [8]. The native point defects formed during the growth process can be

reduced effectively by post-growth annealing treatment at high temperature [9,10]. Moreover, the annealing conditions are important because they affect stoichiometry and influence the films' optical and structural properties. Particularly, the electric and optical properties are sensitive to the annealing atmosphere (i.e., in air, nitrogen, hydrogen, argon, oxygen or in vacuum), as has been studied by several researchers [11,12]. The effects of annealing time (t_{an}) and annealing temperature (T_{an}) in different ambient on ZnO films have been studied previously using many techniques [12,13]. Most of these investigations showed that ZnO films annealed in oxygen atmosphere at $T_{\text{an}} = 900$ °C present high crystalline, optical and electrical properties [9,14]. Post deposition annealing in O_2 ambient at high T_{an} could compensate for V_O and change the conductivity from n-type to p-type [15]. Further, annealing process in O_2 causes lattice rearrangement resulting in relieving of inhomogeneous distribution of strain.

Until recently, few reports show the detailed analysis of the thermal annealing properties of ZnO films grown using alcohols as oxidant. Also, the influence of parameters such as the partial pressure ratio of oxygen and zinc precursors ($R_{V/II}$) on ZnO growth by MOCVD has not been fully investigated. Alcohols have produced very satisfactory results due to non pre-reaction or high reaction rates, in contrast to the other oxygen sources [16,17]. In this paper, we report

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on the annealing and the $R_{V_{II}}$ ratio effects on the optical and vibrational properties of ZnO thin films. The samples were grown by MOCVD using tert-butanol as oxygen source and annealed in oxygen atmosphere at 900 °C. The optical properties of the as-grown and the annealed ZnO films are investigated by Micro-Raman spectroscopy and photoluminescence (PL). Improvement of the optical properties of the annealed films is interpreted in terms of reduction of intrinsic defects and the chemisorption of oxygen. The optical changes in PL spectra were characterized by their different near band emissions with respect to the $R_{V_{II}}$ variation.

2. Experimental details

In this work, ZnO thin films were grown on c-plane sapphire substrates in an MOCVD reactor at atmospheric pressure. Diethyl zinc (DEZn) and tert-butanol are used, respectively, as zinc and oxygen precursors and the carrier gas was N_2 . The bubbler temperatures of DEZn and tert-butanol were kept, respectively, at 17 °C and 28 °C. The ZnO films, with thicknesses ranging from 1.99 to 2.74 μm , were grown at $0.25 \leq R_{V_{II}} \leq 1$. The samples growth conditions, such as growth temperature, precursor flow rates, precursor partial pressures (P_{DEZn} , $P_{\text{t-but}}$) and their pressure ratio ($R_{V_{II}}$), were given in Table 1. After growth, the films were cut into pieces and annealed in oxygen ambient for different times varying from 1 to 6 h. The T_{an} was kept at 900 °C and the oxygen ambient pressure was 1 atmospheric pressure. The Raman spectra were performed at room temperature in backscattering configuration using the 514.5 nm Ar^+ laser line for excitation and the incident laser power was 8 W/cm^2 . The PL experiments were carried out using the 351 nm line excitation from an Argon laser operating at 20 W/cm^2 . The PL spectra were recorded at liquid helium temperature (~ 4 K).

3. Results and discussions

3.1. Raman results

Fig. 1 depicts the room temperature Raman spectra of the as-grown ZnO films grown at various $R_{V_{II}}$ ratios. It shows the well known E_2 high (E_2^H) mode at about 438 cm^{-1} characteristic of the wurtzite phase and corresponding to the vibration of oxygen atoms [18]. The feature at 332 cm^{-1} , which can be seen in the Raman spectra of both the as-grown and the annealed films, is a second-order structure of ZnO and was interpreted as $2E_2(M)$ [19]. In addition, a broad band (BB) ranging from 460 to 600 cm^{-1} , with a maximum at around 520 cm^{-1} , appears in all the Raman spectra of the as-deposited films. The BB intensity increases when the $R_{V_{II}}$ decreases and totally dominates the Raman spectrum of sample S_3 which is grown in Zn-rich condition ($R_{V_{II}} = 0.25$). For comparison, the intensity ratios of the BB to the E_2^H peak are 0.35, 0.72 for films grown at $R_{V_{II}} = 1$ and 0.5, respectively (Table 2). When ZnO films are grown in Zn-rich condition, it is reasonable that the Zn_i and V_O defects exist in the as-grown samples. The large concentrations of these defects may be at the origin of the high intensity of the BB in samples grown in serious oxygen deficiency. The weak feature observed at 379 cm^{-1} was attributed to the A_1 transverse optical (TO) mode of ZnO [20]. This mode is normally forbidden in backscattering geometry, but the presence of residual defects and the little disorientation of the c-axis of the substrate (0.25° in our samples)

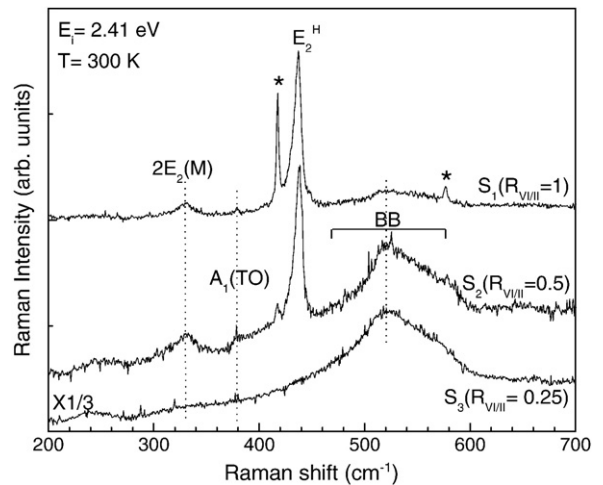


Fig. 1. Room temperature Raman spectra of the as-deposited ZnO thin films grown at various $R_{V_{II}}$ ratios. Observation of the BB at ~ 520 cm^{-1} .

lead to the violation of selection rules and therefore to the appearance of this mode. The A_1 longitudinal optical (LO) mode is not observed in our films, likely because it is subsumed by the strong sapphire E_g mode. The other peaks marked by an asterisk could be ascribed to the sapphire substrate. We note that a small blue shift of the E_2^H mode occurs when the $R_{V_{II}}$ ratio decreases from 1 (S_1) to 0.5 (S_2) (Fig. 1). Since this mode corresponds to the vibration of oxygen atoms, the missing oxygen mass due to a vacancy will blue shift the frequency of the E_2^H mode if these vacancies are present in a large number [21].

The observed BB ($460\text{--}640$ cm^{-1}) was deconvoluted into separated peaks by Lorentzian fitting for a better investigation. As an example, Fig. 2 shows the fitting to the measured Raman lines of sample S_1 . Fitting results show that the BB is deconvoluted into five peaks sited at about 484, 518, 543, 561 and 577 cm^{-1} (for sample S_1). The mode at 577 cm^{-1} is due to the sapphire substrate. However, the modes at 484 and 543 cm^{-1} are attributed to the second-order modes of the longitudinal acoustic (LA) phonons, respectively, from the L point and the M–K line of the Brillouin zone [19,20]. The mode at 518 cm^{-1} , whose intensity vanishes rapidly, and frequency downshifts with increasing t_{an} , is related to crystal defects and/or nitrogen (carrier gas) incorporation into ZnO films. A BB centered at 515 cm^{-1} was also observed by H. Chen et al. in nitrogen doped ZnO films grown by MOCVD on sapphire substrates [22]. They attributed this Raman signal to nitrogen or some defects related local vibration. Also, Bundesman et al. reported that an additional mode at about 512 cm^{-1} appeared in the Raman spectra of Al, Ga, N and Fe-doped ZnO thin films grown by pulsed-laser deposition on c-plane sapphire substrates [23]. The authors suggested host lattice defects as the origin of this mode because its appearance is independent of the ion species. The small frequency upshift of the BB in our case is probably due to the growth conditions and/or the compressive stress in the ZnO films. The weak peak at 561 cm^{-1} , observed in all the fitted Raman spectra, is mainly related to Zn_i atoms [11]. We note that the fitting of Raman spectrum of sample S_3 shows the absence of the modes at 484 and 577 cm^{-1} and the appearance of new modes at 470 and 642 cm^{-1} . The first mode (470 cm^{-1}) may be attributed to crystal defects like V_O and Zn_i and the second mode (642 cm^{-1}) can be related to the

Table 1

Experimental conditions for the ZnO thin films MOCVD growth on sapphire substrates at various $R_{V_{II}}$ ratios.

Sample	$R_{V_{II}}$	Thickness (μm)	Growth temperature ($^\circ\text{C}$)	Flow rate of DEZn (sccm)	Flow rate of tert-but (sccm)	$P_{\text{tert-but}}$ (Pa)	P_{DEZn} (Pa)	Total pressure
S_1	1	1.99	420	30	10	32.2	32	atmospheric
S_2	0.5	2.74	420	30	5	16.1	32	atmospheric
S_3	0.25	2.74	500	60	5	16.1	64	atmospheric

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