

## Raman and Photoluminescence Study of ZnO Films Grown by Chemical Method

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In this paper phonon and emission properties of ZnO films grown by metalorganic chemical vapour deposition (MOCVD) at ambient pressure and by molecular beam epitaxy (MBE) are investigated using Raman and photoluminescence (PL) spectroscopy. It is shown that high-frequency shift of non-polar phonon modes corresponds to elastic compressive strain in the plane parallel to c-axis and is equal to  $3.2 \times 10^{-3}$  and  $2.2 \times 10^{-3}$  for ZnO film grown by MOCVD and MBE, respectively. The possibility of obtaining high-quality ZnO films grown by MOCVD was demonstrated.

**Keywords:** ZnO film, Raman spectroscopy, Photoluminescence, strain, MBE.

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### 1. INTRODUCTION

ZnO films are actively studied due to their unique properties for practical applications in the UV detectors, field emission displays, thin film transistors, solar cells, biosensors and etc.

Up to now, most ZnO films have been prepared by various methods such as magnetron sputtering, impulse laser deposition and MBE. The most perfect crystal structure of ZnO films are obtained by MBE. However, MBE method is quite expensive. Therefore, the development of alternative, more simple and less costly growth method that allows obtaining high-quality ZnO films is an actual problem.

In this paper Raman and PL spectroscopy were used to determine the structural and emission properties of ZnO film grown by modified MOCVD. The properties of this film have been compared with the properties of ZnO film obtained by MBE. Frequency position analysis of nonpolar  $E_2^{high}$  phonon mode allowed estimating the elastic strain and the crystal quality of ZnO films.

### 2. EXPERIMENT

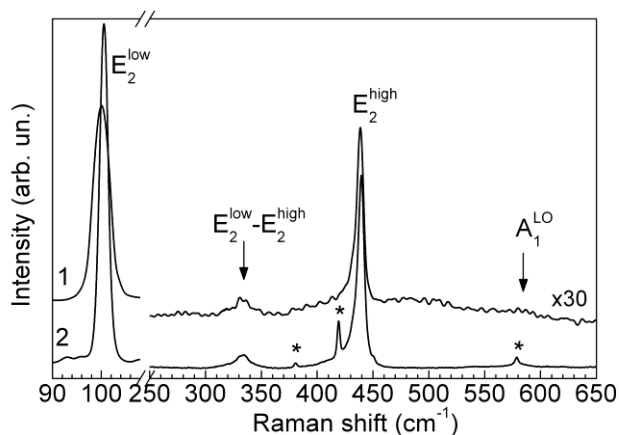
Two types of ZnO films were investigated: first one was grown by MOCVD at ambient pressure on glass substrate (spraying an organic solution of organometallic compounds and heated to 300C glass substrate similar to [1]); second film was grown by MBE on c-plane sapphire ( $Al_2O_3$ ) substrate [2].

Micro-Raman and PL spectra were excited using lines of  $Ar^+/Kr^+$  ion laser (488.0 nm) and He-Cd laser (325.00 nm), respectively. Spectra were collected by Jobin-Yvon T64000 triple spectrometer equipped with a CCD detector and Olympus BX41 microscope with  $\times 100$  objective (NA = 0.90). Spectral resolution was about  $0.15 \text{ cm}^{-1}$ .

### 3. RESULTS AND DISCUSSION

Figure 1 shows the micro-Raman spectra of ZnO films grown by MOCVD and MBE. Phonon modes cor-

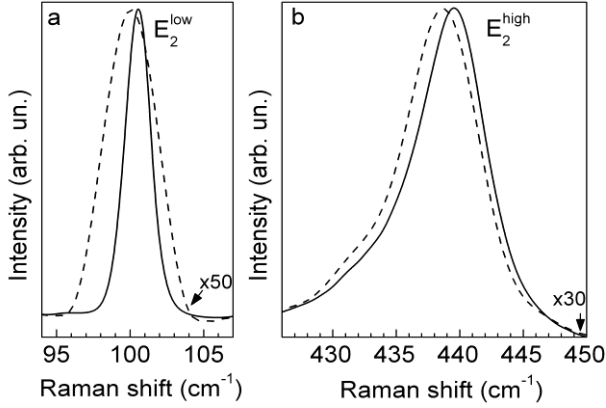
responding to  $E_2^{low}$ ,  $E_2^{high}$ ,  $E_2^{high} - E_2^{low}$  and  $A_1^{LO}$  of ZnO wurtzite crystal structure are present in the Raman spectra of ZnO films. Weak peaks at 332.0 and  $576.0\text{--}580.0 \text{ cm}^{-1}$  correspond to  $E_2^{high} - E_2^{low}$  difference two-phonon and  $A_1^{LO}$  polar modes of ZnO films, respectively.



**Fig. 1** – Micro-Raman spectra of ZnO films grown by MOCVD (curve 1) and MBE (curve 2). Asterisk indicates the sapphire substrate phonon modes at 379.6, 419.2 and  $578.4 \text{ cm}^{-1}$ .  $\lambda_{exc} = 488.0 \text{ nm}$ ,  $T = 300 \text{ K}$

Non-polar  $E_2^{low}$  mode is observed at  $\approx 100.1$  and  $100.6 \text{ cm}^{-1}$  for ZnO films grown by MOCVD and MBE, respectively (Fig. 2a). Low frequency shift of  $E_2^{low}$  mode as compared to the frequency for bulk ZnO ( $\omega_0 = 101.0 \text{ cm}^{-1}$ ) is caused by biaxial compressive strain in the plane perpendicular to the c-axis. The fact that the halfwidth of nonpolar  $E_2^{low}$  mode of ZnO film grown by MOCVD ( $\approx 3.8 \text{ cm}^{-1}$ ) is higher than the halfwidth for ZnO film grown by MBE ( $\approx 1.7 \text{ cm}^{-1}$ ) indicates higher structural quality in zinc sublattices of the latter film [3].

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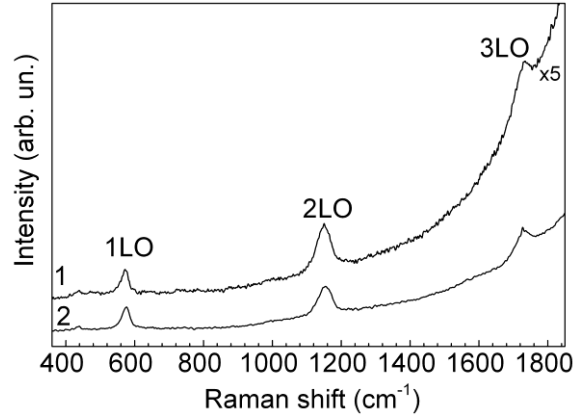
**Fig. 2** – Micro-Raman spectra of ZnO films grown by MOCVD (dash curve) and MBE (solid curve) in the frequency range of  $E_2^{low}$  (a) and  $E_2^{high}$  (b) phonon modes.  $\lambda_{exc} = 488.0$  nm.  $T = 300$  K.

The value of biaxial strain  $\varepsilon_{zz}$  along the c-axis of ZnO films is determined by the frequency shift  $\Delta\omega(E_2^{high})$  [4]:

$$\varepsilon_{zz}^{(\Delta\omega)} = (\omega - \omega_0) / (b - a(C_{33}/C_{13})) = \Delta\omega(E_2^{high}) \cdot K.$$

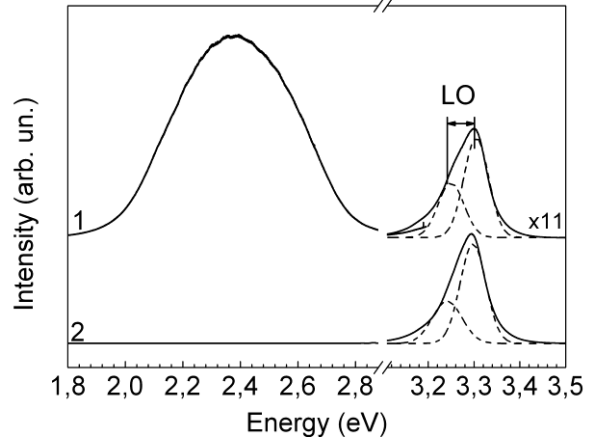
For strain-free ZnO:  $\omega_0 = 437.0$   $\text{cm}^{-1}$  – frequency of  $E_2^{high}$  phonon mode;  $a = -690$   $\text{cm}^{-1}$  and  $b = -940$   $\text{cm}^{-1}$  – phonon deformation potentials;  $C_{13} = 90$  GPa and  $C_{33} = 196$  GPa – elastic constants. The observed high – frequency shift of the  $E_2^{high}$  mode by  $\Delta\omega_{E_2} = \omega - \omega_0 \approx 1.7$  and  $1.2$   $\text{cm}^{-1}$  corresponds to the biaxial compressive strains  $\varepsilon_{zz} \approx 3.2 \times 10^{-3}$  and  $2.2 \times 10^{-3}$  for ZnO films grown by MOCVD and MBE, respectively (Fig. 2b). Using Poisson ratio ( $\varepsilon_{xx}^{(\Delta\omega)} = -\varepsilon_{zz}^{(\Delta\omega)} C_{33} / 2C_{13}$ ), the value of  $\varepsilon_{xx}$  strain perpendicular to c-axis is equal to  $\approx -3.5 \times 10^{-3}$  and  $-2.4 \times 10^{-3}$  for ZnO films grown by MOCVD and MBE, respectively. The halfwidth of  $E_2^{high}$  phonon modes is equal to  $\approx 6.9$  and  $6.0$   $\text{cm}^{-1}$  for ZnO films grown by MOCVD and MBE, respectively. This fact indicates high structural quality in oxygen sublattice for investigated ZnO films (Fig. 2b).

Multi-phonon LO-modes (up to 3LO) on the background of photoluminescence were observed in resonance Raman scattering of ZnO films. These LO modes correspond to an inelastic scattering on  $A_1^{LO}$  phonons of ZnO films (Fig. 3). In resonant Raman spectra, the increase of LO phonons intensity as well as the high order one phonon  $A_1^{LO}$  modes is caused by the Froehlich electron-phonon interaction. The difference of  $A_1^{LO}$  phonon modes frequency for ZnO films grown by MOCVD ( $572.8$   $\text{cm}^{-1}$ ) and MBE ( $575.9$   $\text{cm}^{-1}$ ) as compared to the frequency for bulk ZnO ( $\omega_0 = 574.0$   $\text{cm}^{-1}$ ) might be caused not only by elastic compression strain [5] but also by high concentration of free charge carriers in ZnO films [6]. The intensity ratio of second and first order LO phonon modes  $I_{2LO}/I_{1LO}$  is equal to  $\approx 1.9$  and  $1.2$  for ZnO films grown by MOCVD and MBE, respectively. The obtained values  $I_{2LO}/I_{1LO}$  indicates the high efficiency of electron-LO-phonon interaction for investigated ZnO films [7].



**Fig. 3** – Resonant micro-Raman spectra of ZnO film grown by MOCVD (curve 1) and MBE (curve 2).  $\lambda_{exc} = 488.0$  nm.  $T = 300$  K.

The ultraviolet (UV) emission band with a maximum at  $\approx 3.30$  eV and the halfwidth at  $\approx 60$  eV was registered in PL spectra of ZnO films (fig. 4). This radiation is due to radiative recombination of localized excitons bound to neutral donors and/or acceptor [8]. The higher PL intensity of ZnO film grown by MBE (11 times) as compared to the intensity for ZnO film grown by MOCVD is caused by less amount of nonradiative recombination centers. Low-energy asymmetry of UV PL peak in ZnO films is modeled by two Gaussian contours. The fact that the distance between the maxima of these lines is equal to LO-phonon energy of ZnO indicates the high efficiency of radiative recombination with participation of LO phonons.



**Fig. 4** – PL spectra of ZnO films grown by MOCVD (curve 1) and MBE (curve 2). Dash line – modeling by Gaussian contours.  $\lambda_{exc} = 325.0$  nm.  $T = 300$  K.

The intensive wide PL peak emission at 2.0–2.3 eV in ZnO film grown by MOCVD is also registered. It is associated with intrinsic point defects such as vacancies of oxygen ( $V_O$ ), interstitial atoms of zinc ( $Zn_i$ ) or oxygen ( $O_i$ ) [9].

#### 4. CONCLUSIONS

The phonon and emission properties of ZnO films grown by MOCVD and MBE were investigated by Raman and photoluminescence spectroscopy. The value of

elastic compressive strains and the crystal structure quality in zinc and oxygen sublattices of wurtzite ZnO films were characterized. The possibility of obtaining

high-quality ZnO films suitable for optoelectronic devices by MOCVD technique at ambient pressure was demonstrated.

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