Pulsed laser deposited stoichiometric ZnO thin films

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Abstract—Room temperature free-exciton emission was observed in stoichiometric ZnO epilayers grown on Al₂O₃ substrates by pulsed laser deposition. Absorption and photoluminescence measurements clearly showed the free-exciton emissions at 3.30–3.31 eV. This free-exciton recombination results from the high-quality single-crystalline ZnO epilayers. Temperature-dependent excitonic properties revealed the higher thermal stability of stoichiometric ZnO epilayers with the effective phonon energy, electron-phonon interaction and exciton-phonon coupling of 65.2 meV, 0.093 meV/K and 680 meV, respectively. The strong exciton-phonon coupling has been attributed to the high Fröhlich constant due to the strong localization energy in the stoichiometric ZnO epilayers.

Keywords - ZnO; stoichiometry; free excitons; exciton-phonon coupling; lattice dilation

I. INTRODUCTION

ZnO and related oxide materials (MgO, BeO and CdO) have drawn a considerable attention in recent years due to their suitability for the fabrication of blue to ultraviolet light emitting diodes (LEDs) and exciton- and polariton-based laser diodes (LDs) since the exciton and biexciton binding energies of bulk ZnO material are 60 meV and 15 meV, respectively.¹⁻³ These exciton and biexciton binding energies in epitaxial ZnO based quantum structures have been tuned to 120 meV and 30 meV, respectively.⁴ With the higher oscillator strength associated with these excitons and biexcitons, these features could lead to lower-threshold lasing and higher quantum efficiencies.¹⁻² It has been expected that these promising features of epitaxial ZnO layers will contribute directly to the development of optoelectronic and nanoelectronic devices operating at elevated temperatures. Recently homojunction ZnO LED has been reported with the outstanding properties compared to the GaN LED.¹ However, the reproducibility and stability problems in the homojunction ZnO LED are still the challenges due to the complex role of donor-acceptor pairs and conductivity conversion under the illumination and exposing to room ambient.

Until today, the main challenges facing the ZnO material system are the reproducibility of *p*-type conductivity, clear understanding on the dopant-defect complexes, origin/role of native defects, etc. Basically, all of these difficulties are somehow related to the lack of high-quality single-crystalline ZnO epilayers – responsible for stoichiometry. To obtain

stoichiometric ZnO epilayers, therefore, pulsed laser deposition (PLD) system has been used as the laser ablated plumes interact directly with the substrate, along with the O₂ partial pressure. The O₂ partial pressure, together with the plumes inside the deposition chamber under the high temperature and low pressure, produces O₂ plasma with different species, like, radicals, ions, and atoms. These O₂ plasma species (especially radicals) interact with the ablated plumes and produce a stoichiometric ZnO epilayers. In this paper, stoichiometric ZnO epilayers with excitonic properties even at room temperature have been addressed.

II. EXPERIMENTS

ZnO thin films were deposited on Al₂O₃(0001) substrates by PLD. The Al₂O₃ substrates were degreased chemically prior to loading into the deposition chamber. The Al₂O₃ substrates were then cleaned thermally inside the chamber for 20 min with O₂ partial pressure for 500 mTorr at 600 °C. After the substrate cleaning processes, excimer laser (KrF, 248 nm) was used to ablate ZnO targets for deposition of ZnO layers at the substrate temperature of 600 °C. The laser pulse repetition rate was 5 Hz for the power of 280 mJ.

The ZnO thin layer thickness measured using the alpha-step 200 surface profiler was 0.5–0.7 μm. The surface morphology was assessed by contact mode atomic force microscopy (AFM). The x-ray powder diffraction (XRD) measurements were conducted using a CoKα1 line ($\lambda = 1.7906$ Å). Rutherford Backscattering (RBS) studies were performed with 2 MeV 4He⁺² ions. Photoluminescence (PL) and absorption (UV-Vis) measurements were performed by using the He-Cd laser and Xe lamp, respectively.

III. RESULTS AND DISCUSSIONS

ZnO epilayers deposited on Al₂O₃ substrates showed only the (0002) plane peak in XRD spectra, indicating that the ZnO epilayers are highly crystalline along the *c*-axis. The crystalline quality of ZnO epilayers, however, was further investigated by RBS spectroscopy. Figure 1a shows the random RBS spectrum of ZnO for the layer thickness of 0.45 μm. According to SIMNRA simulation of the RBS spectra, the PLD grown ZnO epilayers were found to be stoichiometric. Surfaces and interfaces of the Zn and O are marked in figure. From this result, it is clear that there are few impurity/contamination in the ZnO epilayers. However, these impurities/defects might be related partially to the Al atoms as diffracted in the RBS spectrum. Therefore, this high-quality

Figure 1. (a) Random RBS spectrum with SINRAM fitted solid line and (b) O_2 pressure dependent Zn/O ratio in ZnO thin layers deposited on Al_2O_3 substrates. The energy of the $^4He^{+2}$ beam was 2 MeV.

ZnO epilayers deposition has been attributed to the active reaction of ablated plumes under the sufficient O_2 plasma species.

Figure 1b shows the O_2 partial pressure-dependent Zn and O atomic ratio of ZnO epilayers measured by using RBS followed by SIMNRA simulations. It is noted that during this optimization, the O_2 flow rate was kept constant for 20~25 sccm. With the increase of O_2 partial pressure, the Zn/O atomic ratio is coming closer to one and almost constant for the O_2 partial pressure range of 500–600 mTorr. If the O_2 partial pressure is increased further, the ZnO epilayers crystalline quality degrades again, possibly due to the higher O atoms/species. It has been reported that the nonstoichiometry in ZnO epilayers is related to the O vacancies and/or Zn interstitials.²

Under the stoichiometric growth conditions, therefore, the surface properties of ZnO epilayers changed from irregular

grains/islands to the ordered hexagons morphology. Figures 2(a) and (b) show the AFM images of nonstoichiometric and stoichiometric ZnO epilayers, respectively. The island/grain in nonstoichiometric ZnO layers, while the uniform hexagons morphology in the stoichiometric ZnO epilayers has been observed. The hexagons are aligned uniformly along the [0001] directions with an approximate dimension of $0.8\sim 1.0 \mu m^2$. As the Zn/O ratio is increased from O rich to the stoichiometric condition, the root-mean-square roughness was decreased from 15 to 4 nm. The change from islands/grains to regular hexagons morphology with the increase of Zn/O atomic ratio has been attributed to an enhanced diffusion of Zn adatoms. This morphology switching in wurtzite ZnO seems to be related to the polarity, because ZnO in opposite polarities shows quite different properties under the same growth conditions.⁵ Under the stoichiometric growth condition, the mass transport causes an initial tiny pit on the surface to grow up to a larger hexagon on the ZnO surfaces.

Figure 3a shows the PL and absorption spectra of ZnO epilayers studied at room temperature. Clear excitonic structure in absorption spectrum has been observed at 3.313 eV. In the PL spectrum, the dominant peak has been observed at 3.303 eV with a subpeak in the shoulder at 3.13 eV. The subpeak has been attributed to the longitudinal (LO) phonon replica.² The sharp luminescence peak near 3.303 eV has previously been reported to be free-exciton emission,^{1,5} that has been reproduced by Chichibu *et. al.* [6]. This bandedge

Figure 2. Atomic force microscopy images of (a) nonstoichiometric and (b) stoichiometric ZnO epilayer. The area scan for both the layers of $10 \times 10 \mu m^2$.

emission is due to the free-exciton recombination,² although it is slightly red-shifted from the absorption peak. This blueshift in absorption spectra has frequently been observed in the ZnO epilayers.⁶ These free excitons observation at room temperature, therefore, reveal the single-crystalline ZnO epilayers deposited on Al₂O₃ substrates.

In order to examine the thermodynamic behavior of free-exciton properties, temperature-dependent PL spectra were measured, and analyzed to determine the nature of the free-exciton peak in the range of 13–300 K. Two types of samples were considered for this purpose: stoichiometric and nonstoichiometric ZnO epilayers. To estimate the peak positions as well as the linewidth, the PL spectra were fitted using the Gaussian equation which was in fairly good agreement with the experimental data. The free-exciton peak energy of ZnO epilayers is gradually decreasing for both the cases. However, the rate of decrease for these ZnO epilayers is different. Figure 3b shows the temperature dependence of the photon energies of ZnO epilayers grown under the

stoichiometric and nonstoichiometric conditions. The PL peak energy is constant at $T < 100$ K and $T < 50$ K for the stoichiometric and nonstoichiometric ZnO epilayers, respectively. With the further increasing of T , however, the peaks redshift gradually for both the samples. The redshift in the semiconductor bandgap with T results from the temperature-dependent thermal expansion/dilation of lattice and carrier-phonon scattering. It has been found that in the temperature range of 13–300 K, Bose-Einstein approximation gives the best fit to the experimental data using the effective phonon energy $\hbar\omega_{LO}$ and the variation of exciton energy with the T by

$$E_T = E_0 - \frac{\lambda}{\exp(\hbar\omega_{LO}/k_B T) - 1} \quad (1)$$

where E_0 is the exciton energy at $T = 0$ K, and λ is a proportional coefficient. The λ value for the stoichiometric ZnO epilayer is 3.2 times higher than that of the nonstoichiometric ZnO epilayers. The estimated values of $\hbar\omega_{LO}$ for the stoichiometric and nonstoichiometric ZnO epilayers were found to be 65 and 35 meV, respectively which are apparently higher than the maximum energy of a lower frequency group of ZnO bulk phonons of ~ 12 meV.⁷ Therefore, these results indicate that the strength of exciton-phonon coupling in the stoichiometric ZnO epilayers is increased in comparison that in the nonstoichiometric ZnO layers.

To clarify the origin of the increased exciton-phonon interaction, the temperature-dependent PL linewidth has been elucidated. The linewidth of PL peak, Fig. 3b, increases monotonically with the increasing of temperature from 13–140 K and is thereafter exponential up to room temperature by the different fashion for the stoichiometric and nonstoichiometric ZnO layers. The temperature dependences of linewidth could be interpreted as a broadening due to the exciton-phonon scattering and the piezoelectric contribution. It has been found that at low temperature ($T < 140$ K) the increase of Γ_T is almost linear with a temperature which indicates the influence of acoustic-phonon scattering. The coupling strength of exciton-acoustic phonon is closely correlated to the deformation potential of solid state materials. However, in temperatures above 150 K, an increase of Γ_T is nearly exponential which suggests that the LO-phonon is included. Disregarding the piezoelectric contribution, the temperature-dependent broadening of the PL peak has been interpreted in terms of the exciton-phonon scattering in different temperature regimes using the following formulation by

$$\Gamma_T = \Gamma_0 + \gamma_{ph}T + \frac{\Gamma_{LO}}{\exp(\hbar\omega_{LO}/k_B T) - 1} \quad (2)$$

where $\hbar\omega_{LO}$ is the energy of a LO phonon, Γ_0 is the inhomogeneous broadening at 0 K, γ_{ph} is the coupling strength of the exciton-acoustic phonon interaction, Γ_{LO} is a parameter related to the strength of the exciton-LO-phonon interaction. It was found that a reasonably good fit of solid lines is obtained for $\gamma_{ph} = 30$ μ eV/K and $\Gamma_{LO} = 680$ and 1450 meV for the stoichiometric and nonstoichiometric ZnO thin films, respectively. The gradual increase of the linewidth in the low

Figure 3. (a) Photoluminescence and absorption spectra measured at room temperature and (b) temperature-dependent PL peak energy and linewidth of ZnO thin layers deposited on Al₂O₃ substrates. The solid lines in Fig (b) are the theoretical fittings. The O₂ chamber pressure for the corresponding stoichiometric and nonstoichiometric ZnO thin layers were considered for 550 and 200 mTorr.

temperature regime up to 140 K is attributed to the exciton scattering with the acoustic phonons while the exponential rise at higher temperatures is attributed to the LO phonons. For comparative studies, all parameters, together with GaN and ZnSe materials at room temperature, have been summarized in Table I.

TABLE I. E is the bandedge energy, λ is a proportional constant, $\hbar\omega_{LO}$ is the effective phonon energy, γ_{ph} is the exciton-acoustic-phonon coupling strength, and Γ_{LO} is that of exciton-phonon. The former three parameters are deduced from Eq. (1), whereas the later two are deduced from Eq. (3).

Material	E (eV)	λ (meV)	$\hbar\omega_{LO}$ (meV)	γ_{ph} (μ eV/K)	Γ_{LO} (meV)	Ref.
ZnO _s	3.30	72.0	65.2	30.3	680	this work
ZnO _{ns}	3.28	22.5	35.6	30.1	1450	this work
ZnO	3.30	20.9	11.4	11.3	876	7
GaN	3.40	121	27.3	15.3	208	12a
ZnSe	2.81	32.1	9.9	64.2	126	12b

s : stoichiometry and ns : nonstoichiometry

Surprisingly, the γ_{ph} values for both the stoichiometric and nonstoichiometric ZnO epilayers are the same, and pretty much similar to the values reported for other semiconductors,⁷⁻⁸ whereas the Γ_{LO} is relatively high. This higher value is probably due to the very high Fröhlich constant (α_F).¹⁰ The α_F strongly depends on the ionic polarization of the crystal, which is related to the static and high-frequency dielectric constants of ZnO material. In principle, higher the Fröhlich constant the higher is the localization energy. The α_F in ZnO epilayers has been calculated to be 1.19 using the relationship of $\alpha_F = 0.43 \times Inf_i + 0.69$.¹¹

IV. CONCLUSIONS

Stoichiometric ZnO epilayers have been demonstrated deposited on Al₂O₃(0001) substrates. Clear excitonic emission was obtained at room temperature. The temperature dependence scattering properties in stoichiometric ZnO thin layers were found to be $\lambda = 72$ meV, $\hbar\omega_{LO} = 65.2$ meV, $\gamma_{ph} = 30$ μ eV/K and $\Gamma_{LO} = 680$ meV. These strong exciton-phonon coupling strengths have been attributed to the higher Fröhlich constant and +c polarity in the ZnO epilayers.

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