

Temperature dependent photoluminescence of epitaxial ZnO films on Si (111) substrates

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High quality epitaxial ZnO films were grown on Si (111) substrates with MgO/TiN buffer layers by PLD. XRD and HRTEM confirm the good quality. PL properties were investigated of temperatures from 83 K to 303 K. Combining the excitons as well as relevant phonon replicas with PL spectra, thermal behaviors of excitonic peak energy, line width, and intensity were analyzed. The yielded band gap of ZnO can be well described by Varshni formula. The extracted thermal activation energy of free exciton (X_A) is 53.2 meV. The peak width of X_A at 83 K is as narrow as 18.7 meV.

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1. Introduction

Among wide band gap semiconductors, ZnO is characterized by its direct band-gap of 3.37 eV at room temperature (RT) and a very large exciton binding energy of 60 meV [1,2]. Owing to the strong exciton binding energy, ZnO-based ultraviolet (UV) opto-electronic devices are expected to be highly efficient and practical. For the ideal applications in excitonic lasers and opto-electronic devices, successful ZnO related p-n devices or advanced multi-quantum-well structures are needed.

To take advantage of the two above structure applications, the one important prerequisite is obtaining high quality or even single-crystalline ZnO films, with excellent optical properties (strong excitonic resonance spectra) and electrical properties (high carrier mobility). The single-crystalline ZnO films which meet above-mentioned requirements are usually grown on expensive and lattice-matched substrates such as ScMgAlO₄, Al₂O₃ and YSZ, etc. [3,4,5]. These attractive results are still inconsistent with the matured Si integrated technology, because of applicability limitation of heteroepitaxial growth among various substrates. Therefore, there are few reports in the literature on the growth and optical properties of "high quality" ZnO films on Si substrates [6-9], and even fewer papers about quantum ZnO films on Si substrates. For the other important prerequisite is high-quality p-type ZnO or advanced structures, there is a necessary facet that

un-doped ZnO film with high carrier mobility and low residual carrier concentration [10]. Furthermore, the epitaxy and the surface atom polarity would influence the doped efficiency, because the number of dangling bonds of each Zn or O atom on growth surface is different from different polarities[11], which resembling surface phenomenon has been demonstrated that Mg doping is much easier on Ga-polar GaN than on N-polar GaN.[12] In addition, the epitaxy un-doped ZnO film and atom impact interface structure greatly affect the multi-quantum-well's efficiency. Consequently, it is very essential to control the crystalline quality and research the photoluminescence (PL) spectra of epitaxy ZnO films on Si before we do p-type doping or quantum-well or other opto-electronic devices.

Very recently [8,9], we have reported an epitaxial n-ZnO/MgO/TiN/n⁺-Si hetero-structured light-emitting diode entirely fabricated by pulsed-laser deposition (PLD), and demonstrated that the high quality epitaxial growth of ZnO films were realized. In this work, we focus on the study of temperature dependent (83 K-303 K) PL properties in these high quality epitaxial ZnO films grown on Si (111) substrates by PLD. Various UV excitonic emissions and their phonon replicas are assigned, and the yielded temperature dependence of excitonic line width, peak energy, and peak intensity are discussed in detail. The revealed exciton related information is very useful for future high-efficiency ZnO-based UV opto-electronic applications.

2. Experimental procedure

ZnO/MgO/TiN/Si films were fabricated by pulsed-laser deposition using a KrF excimer laser ($\lambda=248$ nm, repetition rates of 5 Hz). The focused laser energy density was set at 7 J/cm^2 and the target-substrate distance was optimized to 70 mm. Commercial n^+ -Si (111) (resistivity $\sim 10^{-3} \Omega\text{cm}$) wafers were cleaned for 3 min in a mixed solution of HF : distilled water : ethanol with a volume ratio of 1 : 1 : 10 to remove the surface native oxide layer. Prior to the deposition, the growth chamber was evacuated to the order of 10^{-5} Pa by a turbo-molecular pump. Firstly, a thin TiN layer (~ 5 nm) was obtained through 2 min deposition on Si (111) at 600°C . Secondly, at the same substrate temperature of 600°C , *in situ* deposition of MgO film was carried out for 20 min in the oxygen ambient at 10^{-2} Pa . Then, maintaining the oxygen ambient of 10^{-2} Pa , conventional two-step growth of ZnO was performed, i.e., a 20-min low-temperature ZnO buffer layer growth at 500°C and a high-temperature ZnO was subsequently grown at 700°C for 70 min. More details have been described in our previous work [8].

The crystalline structure of as-grown epitaxial ZnO films were characterized by x-ray diffraction (XRD) (D/MAX-2550V Cu $K\alpha$). A Philips CM200 field emission gun high resolution transmission electron microscope (HRTEM), operating at 200 kV, was used for cross-sectional microstructure characterization. PL

spectroscopy measurements were performed at elevated temperatures from 83 K to 303 K in a Jobin Yvon LabRAM HR 800UV system, excited by the 325 nm line of a 5 mW He-Cd laser.

3. Results and discussion

XRD patterns of the ZnO samples present very strong and sharp ZnO (0002) (not shown here), which indicate good crystallinity of the films [8]. Also the weak MgO (111) peak can be observed. The TiN cannot be detected because it is too thin. The XRD peaks also indicate the out-of-plane lattice relationship [8] as ZnO(0002)//MgO(111)//Si(111).

A cross-sectional HRTEM study is carried out to characterize the interface microstructure of ZnO/MgO/TiN/Si system. In Fig. 1(a), a relatively smooth interface can be observed over the imaged region. The thickness of each layer [Fig. 1(b), denoted by arrows] is about 5 nm (TiN), 25 nm (MgO), 200 nm (ZnO), respectively. We consider that there is an amorphous layer of TiN_xO_y between MgO and Si [Fig. 1(c)] by utilizing TiN target. It should be noted that the interface between ZnO and MgO is atomically sharp without any indication of interdiffusion or an amorphous structure [Fig. 1(d)]. The continuous crystalline feature of this interface layer suggests that layer-by-layer ZnO epitaxial growth is formed.

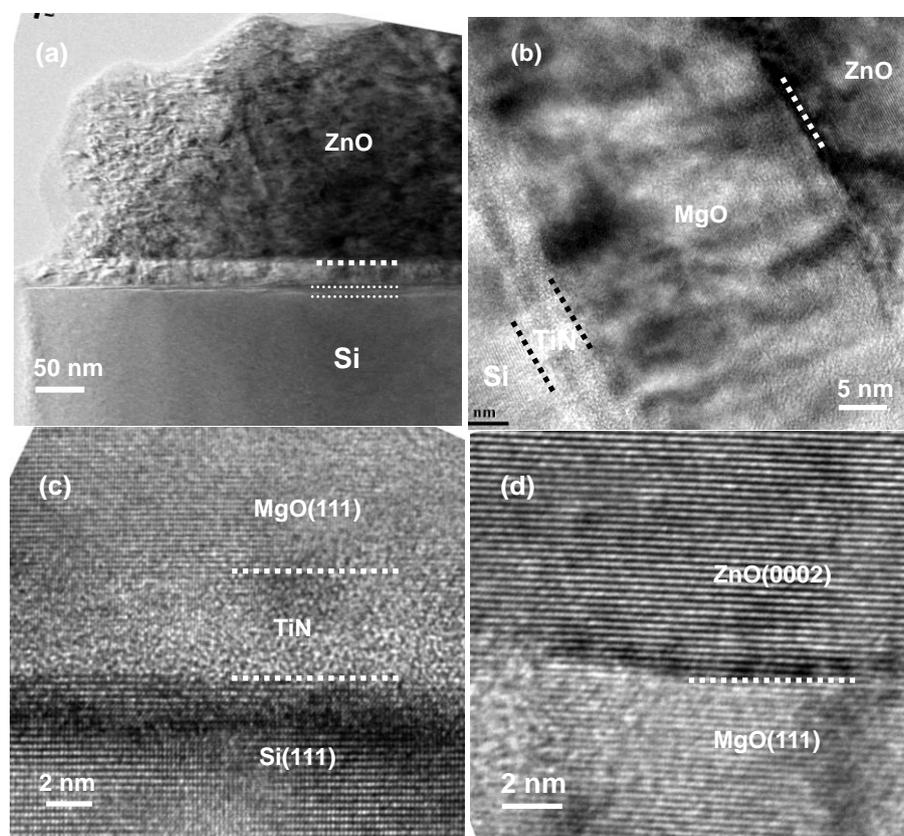


Fig. 1. HRTEM micrograph shows the cross sectional details of ZnO/MgO/TiN/Si interface region. (a) the panorama micrograph; (b) the two interfaces of ZnO/MgO and MgO/TiN/Si; (c) magnified image of MgO/TiN/Si; (d) magnified

image of ZnO/MgO

Generally, the main features of the PL spectra are similar for all ZnO samples, and can be divided into three categories: deep-level emission (DLE) in the visible region, near-band-edge (NBE) emission in the UV region, and the low energy tail extending from NBE emission. As discussed in our previous work [8], these epitaxial ZnO have proven to have good PL properties, where no significant DLEs centered at about 2.2~2.5 eV are detected due to low lattice defects or impurity concentrations while strong NBE emissions centered at about 3.3 eV are observed at RT. Thus in this work, we only focus on the temperature dependences (from 83 K to 303 K) of the strong NBE emission and its nearby low energy tail in the UV region.

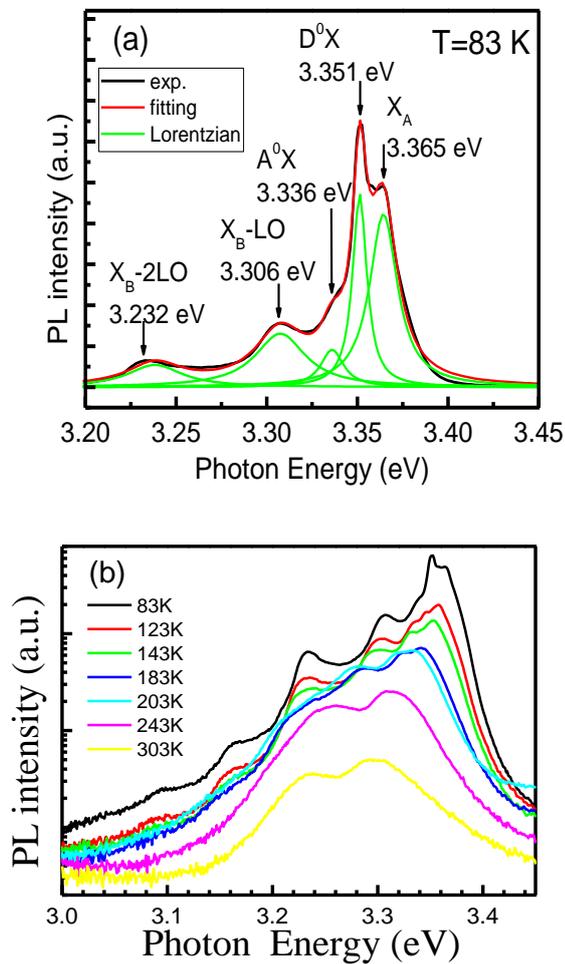


Fig. 2. (a) 83 K PL spectrum (black curve) of ZnO epilayer on Si (111) substrate with MgO/TiN buffer layer, together with Lorentzian deconvolution. (b) PL spectra of ZnO epilayer in the range of 83 K to 303 K

Fig. 2(a) shows the NBE emission at 83 K of the 200 nm thick ZnO epilayer. According to the temperature dependence of peak intensity, the exciton peaks at 3.365 eV, 3.351 eV, 3.336 eV should be identified as A free

exciton (X_A), exciton bound to neutral donors (D^0X), and neutral-acceptor-bound exciton (A^0X), respectively [13]. Researchers usually attribute this particular donor (D^0X) to universal H defects [14], which is the origin of n-type conduction. While for the acceptor (A^0X), its chemical nature still remains undetermined [13]. The low-energy tail extending from the excitonic emission peaks due to the lattice deformation is much reduced, which allows the observation of the phonon replicas of free excitons. At the lower photon energy side, two more peaks are also found at 3.306 eV and 3.232 eV ($\Delta E=74$ meV) and assigned as optical phonon replicas of B free exciton, X_B -mLO ($X_B=3.380$ eV) [13]. The above observations of X_A , D^0X , A^0X and X_B -mLO in PL at 83 K illustrate excellent optical quality of ZnO epitaxial films.

To better understand the nature of the NBE emission, the multi-Lorentzian fittings (Gaussian deconvolution cannot well reproduce the experimental data and consequently is not used) to the experimental spectra have been performed throughout the measured temperature range [Fig. 2(b), where the intensity is displayed on a logarithmic scale], which are in good agreement with the experimental data as demonstrated at 83K in Fig. 2(a). The peak position, width and intensity of all the exciton bands could be estimated and discussed separately at every measured temperature. From the room-temperature PL spectrum, we can see that the free exciton emission is still observable, indicating high crystal quality of the epitaxial ZnO film.

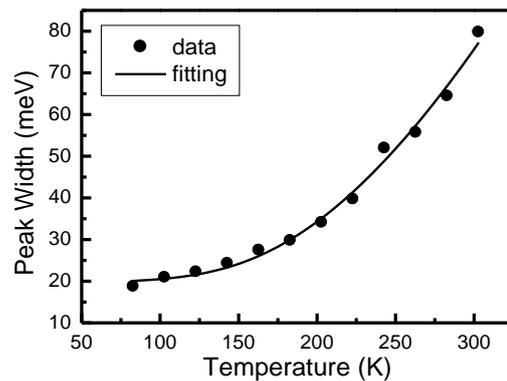


Fig. 3. Temperature dependent peak width (solid points) and the fitting (solid curve) for X_A emission of the epitaxial ZnO thin film grown on Si (111) substrate

Fig. 3 presents the peak width Γ (solid circles) of X_A for the epitaxial ZnO film as a function of temperature (T). The peak width of X_A at RT is 79 meV, which is very much smaller than those of ZnO films grown on matched sapphire (117 meV) [1], on Si (113 meV) [7] and bulk ZnO (115 meV) [15]. From the analysis of spectrum, the

only 18.7 meV of X_A peak width at 83 K can be concluded, which can be comparable with ZnO/Zn_{1-x}Mg_xO multilayers[16]. The peak width Γ of X_A can be analysed as follows. (1) Both the sharp peak and small peak width confirm the high quality and stability of X_A . (2) The peak width Γ smaller, less impurities or defects in the films obviously, the lower residual electrical carrier concentration possessed [7]. The above two points are very favourable for advanced structures such as quantum-well or p-type doping. The emission line broadening of X_A is due to exciton-phonon scattering, which is described by [7]

$$\Gamma(T) = \Gamma_0 + \gamma_{ph}T + \frac{\Gamma_{LO}}{\exp(\frac{\hbar\omega_{LO}}{k_B T}) - 1},$$

where $\hbar\omega_{LO}$ is the energy of a longitudinal optical (LO) phonon, Γ_0 is the intrinsic line width at 0 K, γ_{ph} is the exciton-acoustic phonon coupling constant, Γ_{LO} represents the exciton-LO phonon (Fröhlich) coupling strength, and k_B is Boltzmann constant. The solid curve in Fig. 3 is in good agreement with the experimental data via the least-squares fit using above equation. The yielded result $\hbar\omega_{LO} = 71.98$ meV, which is consistent with the energy difference ($\Delta E = 74$ meV) between the X_B -LO and X_B -2LO, again confirms the accurate assignment of free exciton phonon replicas [Fig. 2(a)]. The fitted values of Γ_0 , γ_{ph} and Γ_{LO} are 18.70 meV, 0.016 meV K⁻¹, and 792 meV, respectively, which are comparable to those (16 meV, 0.033 meV K⁻¹, 435 meV) of free exciton of undoped ZnO grown by ultrasonic spray pyrolysis (USP) [7].

The variations of X_A , D^0X , A^0X and X_B -mLO peak energy against temperature are plotted in Fig. 4(a). The X_A , D^0X , A^0X and X_B -LO emissions systematically shift to lower energy with increasing temperature, whereas X_B -2LO emission almost change little with temperature. From above analysis, the energy difference between the X_A and D^0X was estimated to be ~ 14 meV, which is in fairly good agreement with the reported values for the bulk ZnO [15]. In addition, the D^0X , A^0X , and X_B -2LO emissions appear to be thermally quenched at temperatures above 123 K, 223 K, and 183 K, respectively.

The band gap (E_g) of ZnO can be obtained as the sum of X_A peak energy and exciton binding energy (60 meV). The temperature dependence of band gap (E_g) can be well described by the Varshni formula $E_g(T) = E_g(0) - \alpha T^2 / (T + \beta)$ [17] [see Fig. 4(b)], where $E_g(0)$ is the band gap at 0 K, α is related to the exciton-average phonon interaction and β is closely related to the Debye temperature. The fitted $E_g(0)$ of 3.432 eV, agrees quite well with the band gap value of 3.437 eV for bulk ZnO or Zn_{1-x}Mg_xO at 0 K [18-20],

which indicates that the band tail effect due to the lattice deformation can be neglected. This also implies the good quality of the epitaxial ZnO film grown by PLD. The fitted α and β are 0.00448 eV/K and 506 K, respectively, which are similar to those (0.005 eV/K and 442 K) of ZnO fabricated by a sol-gel method [6].

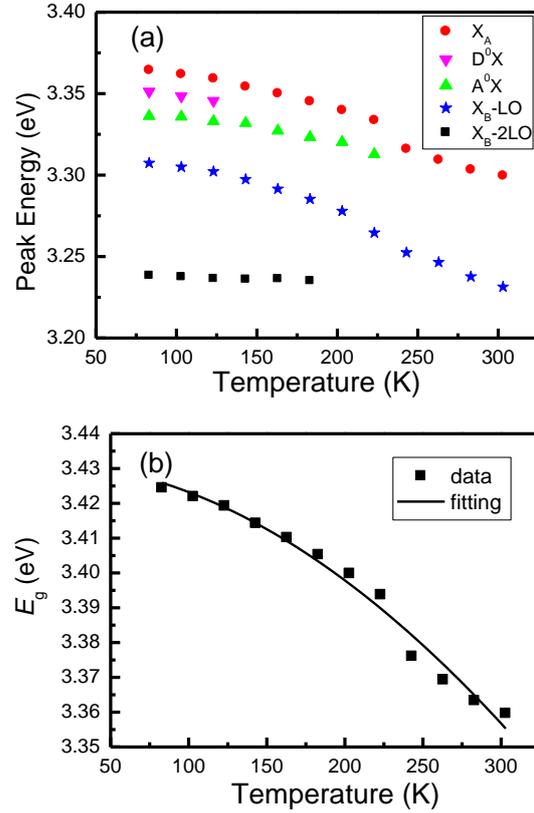


Fig. 4. (a) Temperature dependence of PL peak energy for various excitons assigned, (b) The band gap E_g (solid squares) calculated from X_A , as a function of temperature. The solid curve denotes the fitting using Varshni formula

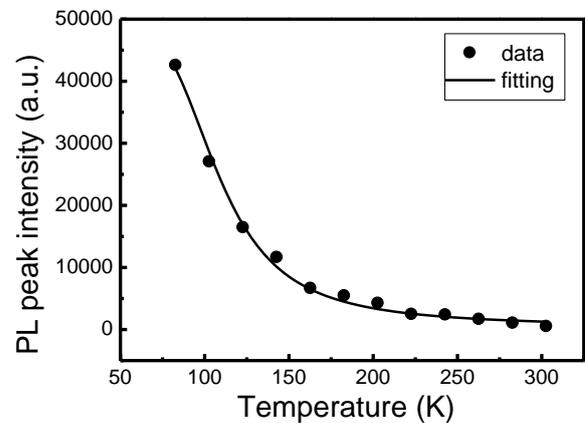


Fig. 5. Temperature dependence of X_A peak intensities (solid circles) for the epitaxial ZnO thin film, as well as the fitting (solid curve)

Fig. 5 shows the X_A peak intensities of NBE emissions versus the temperature. The intensity of X_A decreases dramatically with increasing temperature. The thermal behavior of peak intensity I_{PL} can be well described by the equation of $I_{PL}(T) = I_0 / [1 + C \exp(-E_a/k_B T)]$ [6], where E_a is the activation energy in the thermal quenching process, I_0 and C are constants. The obtained thermal activation energy E_a is ~ 53.2 meV, which is very close to that of ZnO powder (~ 55 meV) [21] and the binding energy (60 meV) of free exciton in single crystal ZnO. Above analysis self-consistently explains the existence of X_A emission contribution in PL spectrum at RT with thermal energy of 26 meV.

4. Conclusions

In summary, the crystalline structure and temperature dependent PL properties of epitaxial ZnO films grown on Si (111) substrates by PLD are investigated. XRD and HRTEM confirm the good crystallinity of the ZnO epilayers. We assigned excitonic bands of X_A , D^0X , A^0X and X_B -mLO in the PL spectrum at 83 K, and also studied their thermal behaviors in the range from 83 K to 303 K through Lorentzian deconvolution. The line width broadening of X_A emission with increasing temperature is due to exciton-phonon scattering. The temperature dependence of band gap of ZnO (or X_A peak energy) is found to be well described by the Varshni formula. Also the thermal activation energy of X_A is estimated to be about 53.2 meV. The peak width of X_A at 83 K is as narrow as 18.7 meV. The analysis results of activation energy, width, and intensities, indicate the crystal quality and UV luminescence efficiency of ZnO films on Si substrates, thus provide an experimental basis for future ZnO-based excitonic device application.

Acknowledgments

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