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Time-resolved and time-integrated photoluminescence in ZnO epilayers grown on $Al_2O_3(0001)$ by metalorganic vapor phase epitaxy

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We report on photoluminescence (PL) spectra of ZnO films grown by low pressure metalorganic vapor phase epitaxy. For PL measurements, high quality ZnO thin films were epitaxially grown on $Al_2O_3(0001)$ substrates. Time-integrated PL spectra of the films at 10 K clearly exhibited free A and B excitons at 3.376 and 3.382 eV and bound exciton peaks at 3.360, 3.364, and 3.367 eV. With increasing temperature, intensities of the bound exciton peaks drastically decreased and a free exciton peak was dominant above 40 K. Furthermore, time-resolved PL measurements at the free exciton peak were carried out at room temperature. The decay profiles were of double-exponential form, and the decay time constants of 180 ps and 1.0 ns were obtained using a least-square fit of the data. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1461051]

There has been great interest in the growth and optical characterizations of ZnO thin films for ultraviolet (UV) photonic device applications.[1,2] Compared with other wide-band-gap materials, ZnO has a larger exciton binding energy (~60 meV),[3] which provides more efficient excitonic emissions at room temperature. The promising optical properties of ZnO films, including stimulated emissions at room temperature have recently been reported.[4,5] Although spectral photoluminescence (PL) of ZnO epilayers have been examined, a complete understanding of the recombination mechanism of carriers requires both temporal and spectral PL measurements.

Time-resolved PL (TRPL) is a nondestructive and powerful technique for the optical characterization of semiconductor thin films. The exciton lifetime, an important parameter related to material quality and device performance, can be measured by TRPL spectroscopy. Carrier dynamics investigated using time-resolved PL can also be used to improve the performance of optical devices. Despite the importance of TRPL measurements, TRPL behavior in ZnO films is not well understood. Only temporal PL from the electron-hole plasma (EHP) state in ZnO films grown by molecular beam epitaxy (MBE) has been reported.[6]

Typically, MBE or pulsed laser deposition (PLD) have been employed for the epitaxial growth of ZnO films.[1,2,4,5] In the case of the growth of other semiconductors, however, metalorganic vapor phase epitaxy (MOVPE) has been widely used since (MOVPE) has many advantages for manufacturing devices. In MOVPE growth of ZnO films, Zn precursors are highly reactive with oxygen and water vapor so that premature reaction in the gas phase occurs easily, resulting in the formation of white powders which degrade film quality.[7] Due to difficulty in the growth of high quality ZnO films using MOVPE, only a limited amount of research on vapor phase epitaxial growth and optical characterizations of ZnO thin films has been conducted.[7–9] As previously reported, however, high quality ZnO films were grown by introducing low pressure growth and a cold-wall reactor which has two separate inlets for the reactants.[10,11] In this article, we focus on spectral and temporal PL measurements of high quality ZnO epilayers grown by the MOVPE technique.

ZnO epilayers were grown on $Al_2O_3(0001)$ substrates using a horizontal type, low pressure MOVPE system. Diethylzinc (DEZn) and oxygen were employed as the reactants for film growth, and argon was used as a carrier gas. Details on the conditions of film growth have been previously reported.[10] In this research, low temperature growth of a very thin ZnO buffer layer was also employed, which significantly improved the film quality. XRD rocking curve data of as-grown films exhibited full width at half maximum (FWHM) values of 0.04°–0.05°, indicating high crystallinity of the ZnO films.[11] In addition, in-plane alignment in the films was confirmed using XRD pole figure analysis.

For optical characterizations of the films, both the time-integrated PL (TIPL) and TRPL of the ZnO films were measured. TIPL measurements were performed using a continuous wave He–Cd laser (325 nm) as the excitation source. Details on the TIPL measurements have previously been reported.[8,10,11] A TRPL measurement system consists of a femtosecond Ti:sapphire oscillator, a homebuilt multipass Ti:sapphire amplifier operating at 5 kHz, a frequency tripler, and a time correlated single photon counting system employing a microchannel plate photomultiplier tube. The fundamental output of the Ti:sapphire amplifier at 800 nm was frequency tripled to 267 nm (4.65 eV), and used as an excitation light. The instrumental response of the entire system was 39 ps (FWHM), providing ~8 ps time resolution with deconvolution.

High resolution PL spectra of ZnO films were measured at 10 K as shown in Figs. 1 and 2. At 10 K, near-band-edge emission shows a shoulder at 3.382 eV and five distinct

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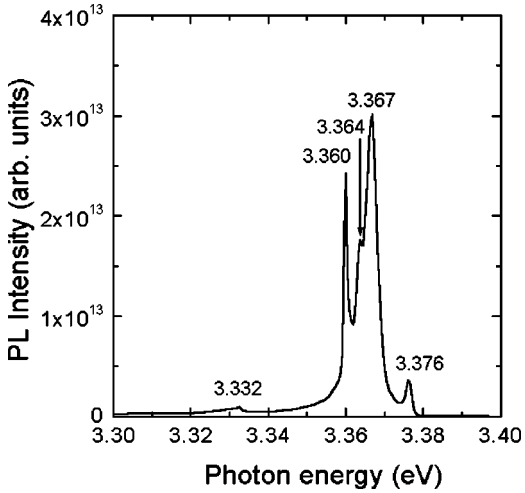

FIG. 1. PL spectrum of ZnO grown on $Al_2O_3(0001)$ using a thin ZnO buffer layer at 10 K. From the PL spectrum, five distinct peaks were observed at 3.376, 3.367, 3.364, 3.360, and 3.332 eV. FWHM values of the peaks are in the range of 1–3 meV.

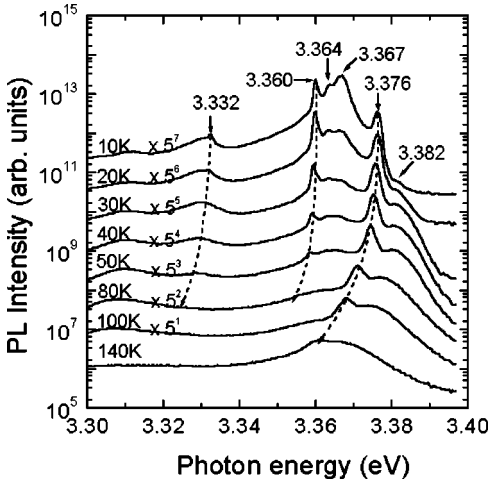

FIG. 2. Temperature-dependent PL spectra of ZnO grown on $Al_2O_3(0001)$. As the temperature increased from 10 to 40 K, the intensities of the free exciton transitions at 3.382 and 3.376 eV observed at 10 K increased while those of the bound exciton peaks at 3.367, 3.364, and 3.360 eV decreased. The bound exciton peaks disappeared above 100 K and only free exciton peaks were observed.

peaks at 3.376, 3.367, 3.364, 3.360, and 3.332 eV with (FWHM) values of 1–3 meV. Among the PL peaks, the dominant emission peaks at 10 K were observed at 3.360–3.367 eV. These peaks are tentatively attributed to the exciton transitions (D^0X) bound to neutral donors and their excited states. The separate bound exciton peaks have previously been observed only for high quality bulk single crystals.[12] For single-crystalline ZnO, the bound exciton peaks have been observed at 3.366, 3.364, 3.361, and 3.357 eV.[12] Slight differences in the peak positions are presumably due to strain induced from the lattice mismatches between the ZnO film and $Al_2O_3(0001)$ substrate.[8] It is also noted that the PL peak at 3.332 eV is similar to that observed at 3.322 eV for bulk ZnO, which has been attributed to a two electron transition.[12] The PL peak at 3.376 eV and the shoulder at 3.382 eV are tentatively ascribed to free exciton peaks since transmission spectra of ZnO single crystals at 4.2 K exhibited strong absorption peaks at 3.378 and 3.386 eV.[13]

Figure 2 shows temperature-dependent PL spectra of the films. As the temperature increased up to 40 K, the intensities of the free exciton peaks increased while the bound exciton peak intensities decreased. The bound exciton peaks disappeared at temperatures above 100 K. This presumably results from decomposition of bound excitons to free excitons due to the increased thermal energy, which strongly supports the argument that the emission peaks at 3.376 and 3.382 eV are attributed to free A and B excitons, respectively.[14] Previous research has reported that ZnO films deposited directly on sapphire substrates generally exhibited only a strong bound exciton peak, presumably due to high concentration of defects in the layers. However, the observation of free exciton peaks from the films grown on ZnO buffer layers in this research strongly suggests that the initially grown buffer layers suppress formation of defects responsible for the bound exciton peaks.

Since most optical devices are used at room temperature, fundamental carrier recombination dynamics at 300 K should be investigated to understand radiative recombination mechanisms. Room temperature TIPL of the ZnO film with the excitation wavelength of 267 nm is shown in Fig. 3(a). A strong PL emission band is observed at 3.26 eV, and its linewidth (120 meV) is comparable with the 117 meV reported for a ZnO film grown by MBE method.[15] Deep-trap emission in the visible region is negligible even at room temperature.

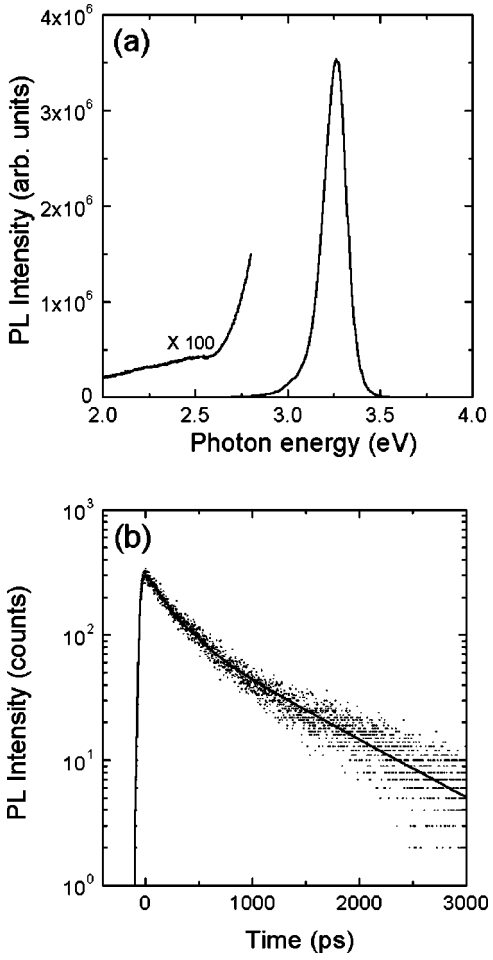

FIG. 3. Time-integrated (a) and time-resolved (b) photoluminescence of a ZnO film at room temperature. In TRPL, the solid line shows the result of a double-exponential fit to the data. Decay time constants for the fit are 180 ps and 1.0 ns.

TRPL of the ZnO film was measured at the 3.26 eV free exciton band. Since the excitation energy of 4.65 eV is far above the room temperature band gap, the excitation first undergoes thermalization to form an exciton, which will further relax to a $K=0$ state before it radiates.[16] The TRPL in Fig. 3(b) shows an instrument-limited rise, implying that these relaxation processes are complete within a few picoseconds at room temperature.[6] A double-exponential function without a rise component fits well the decay profile with a reduced chi square value, χ_r^2, of 1.37 compared with a single exponential fit with χ_r^2 of 7.6. The double-exponential behavior strongly suggests that two different decay or capture processes are involved in the emission although the exact mechanism is not clear yet.

Time constants from the fit are 180 ps and 1.0 ns with relative amplitudes of 2.8 to 1, respectively. The short time constant is comparable to the recombination lifetimes of 245–320 ps at 2 K for free excitons in a bulk ZnO crystal prepared by hydrothermal process although the long decay time has not been reported.[17] Generally a measured PL decay time (τ_{PL}) is shorter than the radiative lifetime (τ_R) since τ_{PL} is determined not only by radiative decay but also by nonradiative decay, related by $\tau_{\mathrm{PL}}^{-1}=\tau_R^{-1}+\tau_{\mathrm{NR}}^{-1}$, where τ_{NR} is nonradiative lifetime.[18] PL lifetime in a semiconductor varies significantly depending on sample purity and preparation, since τ_{NR} includes nonradiative processes such as capture by deep traps and multiphonon emission. A radiative lifetime can be calculated by:[19] $\tau_R=2\pi\epsilon_0 m_0 c^3/ne^2\omega^2 f$, where n is the refractive index, f is the oscillator strength, and m_0, ϵ_0, c, and e are fundamental physical constants with their usual meaning. By using $\omega=4.95\times10^{15}$ s^{-1} and $n\sim2.4$ for ZnO,[20] τ_R is $\sim0.91/f$ ns. For bound excitons with $f\sim1$ as upper limit, the radiative lifetime is estimated to be ~1 ns. In contrast, free excitons having low oscillator strength are expected to exhibit very long lifetimes. The discrepancy between the measured values of PL decay time and calculated radiative lifetime is presumably due to nonradiative relaxation processes competing with the radiative recombination.

In conclusion, from the PL spectra of ZnO thin films grown using ZnO buffer layers, free exciton transitions at 3.376 and 3.382 eV and distinct bound exciton peaks at 3.360, 3.364, and 3.367 eV were observed at 10 K, indicating high optical quality of the films. Furthermore, time-resolved PL at a free exciton band was measured at room temperature, which clearly shows a biexponential decay with lifetimes of 180 ps and 1 ns giving a good fit to the data.

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