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Emission from the higher-order excitons in ZnO films grown by laser molecular-beam epitaxy

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Epitaxial ZnO thin films were grown by laser molecular-beam epitaxy on lattice-matched $ScAlMgO_4$ substrates following the deposition and annealing of suitable buffer layers. The samples were characterized by low-temperature photoluminescence (PL), absorption, and reflectivity measurements. PL from higher order ($n=2$) excitons (A exciton) was observed at temperatures lower than 40 K. The absorption spectrum contained lines and the reflection spectrum exhibited anomalies that were assigned to the excited-states ($n=2,3$) of A and B excitons. The optical quality could be improved dramatically by using annealed ZnO or MgZnO buffer layers. [DOI: 10.1063/1.1748847]

Zinc oxide (ZnO) is now a material of established interest for potential applications in optoelectronic devices, following the demonstration of optically pumped laser action. Extensive work is now in progress in many laboratories[1–11] aimed at establishing acceptor doping in ZnO. One of the problems that needs to be solved to successfully achieve *p*-type doping is the realization of material with a very low background electron concentration in order to avoid the compensation effect. Here, we briefly review current progress in epitaxial growth from the viewpoint of the optical properties of the material. Absorption and photoluminescence (PL) are sensitive and nondestructive techniques for the detection of impurities or defects. Many studies of the optical properties of ZnO single crystals have been reported, dating back to the 1960s.[12–15] The optical properties of these bulk crystals can be used as a benchmark against which epitaxial films may be compared. Desirable characteristics that need to be achieved in epilayers include: (1) the spectrally resolved fine structure of the exciton states (i.e., the A and B excitons), (2) the observation of free excitonic PL at temperatures lower than 10 K, and (3) the observation of spectroscopic signatures associated with higher order ($n\geqslant 2$) free excitons. Difficulties in achieving some of these criteria have been solved during work to improve other wide-gap semiconductors,[16] such as GaN or ZnSe. In 2000, Chen *et al.* published a seminal letter[17] reporting on 4 K PL and reflection studies of heteroepitaxial ZnO layers. They observed a PL line assigned to the A-free exciton and successfully suppressed the broadening of excitons well below the spin-orbit splitting of the valence bands. This gave rise to a well-structured reflection spectrum. We found that epilayers grown on a lattice-matched $ScAlMgO_4$ (SCAM) substrates exhibited improved reflection spectra and their transmission spectra were also of higher quality.[18] More recently, the quality of films grown on SCAM have been found to be dramatically improved by the additional insertion of an annealed buffer layer, as evidenced by the observation of persistent reflection high-energy electron diffraction oscillations (cf. Fig. 2 of Ref. 19).

In this letter, we report the observation of emission and reflectivity anomalies from $n\geqslant 2$ excitons in these state-of-the-art samples, implying that the third improvement criteria listed earlier has been achieved. For more unambiguous spectroscopic assignment of the PL, transmission spectra are also presented by preparing a sample that was grown on an $Mg_{0.15}Zn_{0.85}O$ buffer layer. The alloyed buffer layer is transparent in the wavelength region of interest.[20]

The ZnO layers studied here were either 100- or 500-nm-thick epilayers grown in a laser molecular-beam epitaxy chamber at 950 °C under 1×10^{-6} Torr oxygen flow. A single crystal ZnO target was ablated by KrF excimer laser pulses and the substrate was (0001) SCAM. 100-nm-thick buffer layers of either ZnO or $Mg_{0.15}Zn_{0.85}O$ were grown at relatively high temperature (650 °C) and were annealed at 1000 °C for 1 h in the growth chamber before the epitaxy of ZnO began. A full description of the sample growth technique is beyond the scope of this letter; details have been given previously in Ref. 19. The samples were then placed in an optical cryostat. The source for the PL measurements was the 325 nm line from a He–Cd laser and the source for the transmission and reflection measurements was a xenon filament lamp.[18,21]

Figure 1(a) shows the 5 K reflection spectra of ZnO epilayers, both with and without[18,22] annealed buffer layers. There are several distinct reflectivity anomalies in the exci-

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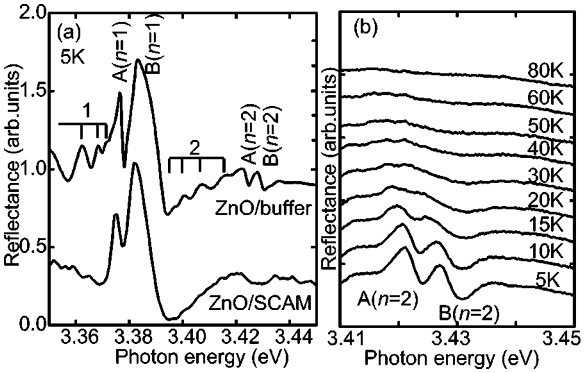

FIG. 1. (a) 5 K reflectance spectra in ZnO grown directly on a SCAM substrate (ZnO/SCAM) and on a buffer layer (ZnO/ZnO buffer). Higher-order excitons A ($n=2$) and B ($n=2$) can be clearly observed in sample with the ZnO/ZnO-buffer layer. (b) The temperature dependence of the reflectivity anomalies.

ton resonance region, the minimum energies of which are 3.378, 3.394, 3.425, and 3.431 eV. These have already been assigned to the $n=1$ states of the A- and B-free excitons and the $n=2$ states of the A and B excitons, respectively.[23] On the other hand, the spectral signatures of these excited-state excitons were hardly observed from a ZnO epilayer grown without a buffer layer [Fig. 1(a)]. Reflection spectra around the $n=2$ exciton resonance, measured as a function of temperature, are also shown in Fig. 1(b). These distinct anomalies persisted up to a temperature of 60 K. Moreover, we observed two oscillatory structures in the energy regions between 3.35 and 3.38 eV and between 3.40 and 3.42 eV (numbered comb marks maxima in Fig. 1). Some Fabry–Pérot modes can be observed, just below the A ($n=1$) exciton energy (3.35–3.38 eV), which are due to multiple reflections.[24] We conclude from this that the coherence of the film thickness is better in the case of the sample with a buffer layer. It is well known that the refractive index is critically dependent on the exciton energy[25] in the exciton resonance region where the dispersive effect is dominant, and therefore the series of peaks are not exactly equidistant.

Further evidence of an improvement in the sample quality was provided by the PL measurements. Figure 2 shows the PL spectra from an epitaxial ZnO/ZnO buffer film recorded at nine different temperatures. As shown in the inset, the PL spectrum at 5 K showed bound exciton peaks and also a variety of lines originating from free excitons most notably the excited-state A exciton. For a detailed assignment of the PL spectra, the transverse exciton energies of the A ($n=2$) and B ($n=2$) states must be known. To achieve this, the transmission spectra need to be measured. However, the ZnO buffer layer is not transparent to the wavelength region of interest, so we tried replacing the buffer layer with a layer of MgZnO. This alloy system has long been used as a barrier layer for ZnO-based quantum wells.[26]

The 5 K absorption, the reflection, and the PL spectrum of the ZnO/MgZnO-buffer/SCAM material are shown in Fig. 3. The structure of the sample is shown schematically in the inset. No correction was made for the reflection loss in the absorption spectra. It should be noted that the peak value of transmission dip for the B ($n=1$) exciton is thought to be above the detection limit, due to the contribution from the Urbach tail absorption of the MgZnO buffer layer. We could

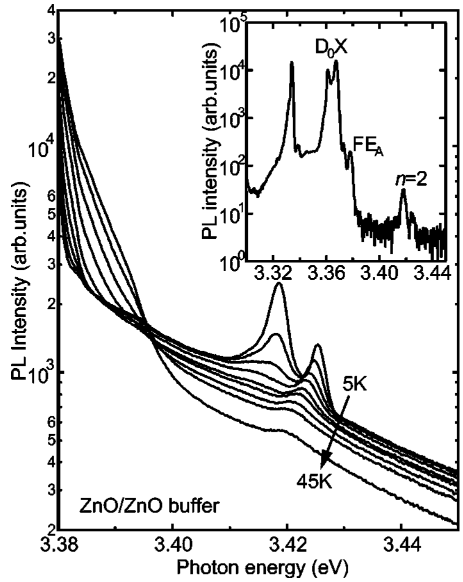

FIG. 2. Temperature dependence of the PL structures at the resonance energy of the excited-state excitons (on a logarithmic scale). The measurement temperature was varied from 5 to 45 K, with 5 K increments. The inset shows a 5 K PL spectrum near the band gap energy region.

also observe the signatures from $n \geqslant 2$ excitons in the spectra. From a comparison between the PL and the transmission spectra, the PL line at 3.425 eV was assigned to the radiative recombination of the A ($n=2$) exciton, while the other line at 3.418 eV has an extrinsic origin; its detailed assignment has not been settled yet. The main absorption peaks can be divided into two classes; the sharp peaks due to intrinsic excitonic absorption [e.g., the C ($n=1$) exciton peak at 3.436 eV] and a broad peak due to an exciton-phonon complex, which is labeled "*L*." The energy separation of the *L* band from the ground-state exciton is close to the LO phonon energy of 72 meV. It is well known from the selection rules for optical transitions that A and B excitons have large

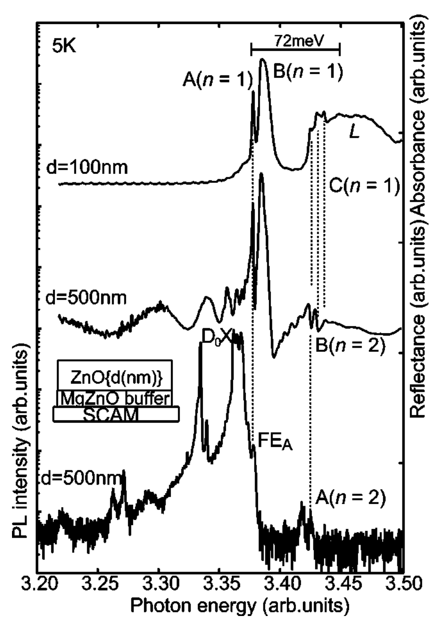

FIG. 3. 5 K absorbance, reflectance, and PL spectrum (from top to bottom) of the sample with the MgZnO buffer. The inset shows the sample structure, with different thicknesses of the ZnO layer [d(nm)]. The growth temperature of these samples was 950 °C.

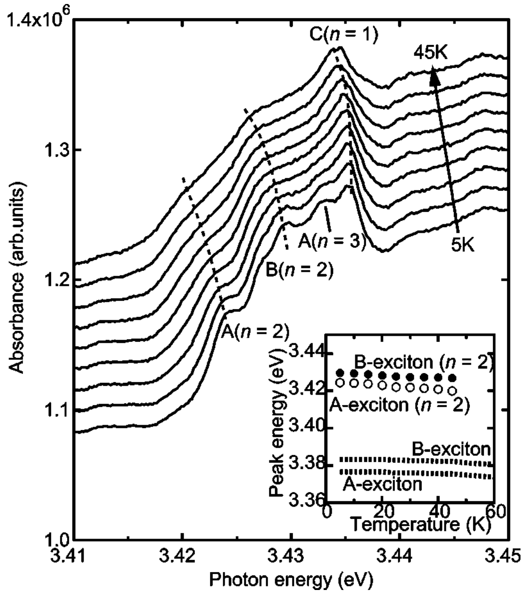

FIG. 4. Temperature dependence of the higher-order exciton absorptions for the sample shown in Fig. 3. The energies of the $(n=2)$ A excitons (open circles) and B excitons (closed circles) are plotted against temperature in the inset. The ground state energies are also shown by the broken lines.

oscillator strength for $E\perp c$ polarization and that the C exciton has a large oscillator strength for $E\parallel c$ polarization. Since all of our samples are c axis oriented, it is reasonable that the C-exciton peak is weakly observed.

The temperature dependence of the absorption structures relating to the higher order excitons is shown in Fig. 4. The $n\geqslant 2$ excitons could exist up to temperatures as high as 45 K. This is significantly lower than the upper bound temperature derived from reflectivity measurements, suggesting that the sample quality became inferior if a MgZnO buffer was introduced. The peak energy positions (open and closed circles) for the A $(n=2)$ and B $(n=2)$ excitons are plotted against the temperature in the inset of Fig. 4. It was found that the temperature-induced shifts ran in parallel to those for the A $(n=1)$ and B $(n=1)$ excitons.

In summary, we have presented the results of low-temperature PL, reflection, and transmission studies for epitaxial ZnO films grown on atomically smooth, lattice-relaxed ZnO or MgZnO buffer layers. Sharp PL and absorption lines and distinct reflectivity anomalies, that were assigned to free A and B $(n=2)$ excitons, provided evidence of improvements in both the crystalline coherence and the concentration of defects and impurities within the films. The absorption and reflection spectra also exhibited lines and anomalies respectively that could be assigned to the excited states $(n=2,3)$ of A and B excitons. The maximum temperatures for the observation of $n=2$ exciton-splitting were 60 K in the reflection spectra and 45 K in the absorption spectra, respectively. The use of lattice-matched SCAM substrates, and particularly of annealed buffer templates, greatly improved the crystalline quality as well as the optical properties of the epitaxial ZnO layers. Such an improvement is favorable from the viewpoint of optoelectronic applications such as current-injected light-emitting diodes.

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