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Exciton spectra of ZnO epitaxial layers on lattice-matched substrates grown with laser-molecular-beam epitaxy

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Optical properties in undoped-ZnO epilayers grown by the laser-molecular-beam epitaxy method on lattice-matched ScAlMgO₄ substrates were investigated. The absorption spectrum at 5 K has two sharp peaks, both of which are attributed to resonances of A and B excitons, which reflect a small nonradiative damping constant of excitons as well as high film crystallinity accomplished by the virtue of lattice matching. The coupling strengths of exciton-acoustic phonon and of exciton-longitudinal-optical phonon were directly determined from the temperature dependence of exciton absorption spectra independently for A and B excitons, which are close in energy and obey the same selection rule for each other. © 2000 American Institute of Physics. [S0003-6951(00)02924-7]

Recently, a wide-gap semiconductor ZnO has attracted considerable attention for such applications as ultraviolet light-emitting diodes and laser diodes. The large exciton binding energy (59 meV¹) permits excitonic recombination well above room temperature (RT). Room temperature lasing has been experimentally confirmed.²⁻⁴ We have observed optically pumped efficient lasing in ZnO epilayers grown on sapphire(0001) substrates by using laser-molecular-beam epitaxy (L-MBE) even at RT owing to the lattice mismatch between ZnO and sapphire (18%).^{2,3,5} Namely, this is the combined effect of cavity formation with hexagonal nanocrystals as well as exciton nature. A lower pumping threshold can be expected, in principle, if an exciton-related recombination rather than a recombination of an electron-hole plasma is used. A representative example of the latter is an In_xGa_{1-x}N-based laser diode.⁶ Such observations indicate that an exciton-related recombination process can be utilized as an optoelectronic device operatable at RT. Therefore, precise determination of the excitonic parameters is important in terms of achieving the fabrication of a high quality material because excitons are a sensitive indicator of material quality. The epilayer on sapphire, however, is not suitable for detailed study of the excitonic properties because inhomogeneous broadening of exciton linewidth is quite large, and the splitting of A and B excitons cannot be observed. In order to realize the above mentioned goal, crystallinity of the epilayer must be improved. Indeed, several efforts are currently being made to improve the crystallinity by inserting a MgO buffer⁷ or by adopting MgAl₂O₄(111) substrates⁸ whose misfits are smaller than that of sapphire. It would be

interesting to adopt ScAlMgO₄ (0001; SCAM) as a substrate whose lattice constant matches that of ZnO by 0.09% because both a reduction in the exciton broadening parameter and higher crystallinity could be expected. Indeed, not only a reduction in residual electron concentration but also an improvement in crystallographic quality compared with those in the case of sapphire substrates⁹ have been confirmed by atomic force microscopy and x-ray diffraction measurements. The full width at half maximums (FWHMs) of in-plane and out-of-plane rocking curves are less than 0.02° and 0.01°, respectively, in ZnO films grown on SCAM substrates. When ZnO films were grown on sapphire, these widths were larger than 0.09° and 0.04°, respectively.⁹ Correspondingly, the relevant optical spectra are able to give detailed information on the excitonic properties in its resonance region. As a result, the exciton-related parameters could be determined in detail.

Here, temperature dependence of absorption spectra is reported in undoped ZnO epilayers on SCAM substrates fabricated by the L-MBE method in order to elucidate the basic optical properties. We successfully estimated the coupling strengths of the exciton-acoustic phonon and of the exciton-longitudinal-optical (LO) phonon independently for A and B excitons by analyzing the temperature dependence by virtue of their improved optical properties.

Epilayers of ZnO were grown on SCAM(0001) substrates with L-MBE under high vacuum conditions.¹⁰ KrF excimer laser pulses were impinged onto ZnO ceramic target (99.999%) located 5 cm away from the substrate surface. The films were grown at a temperature of 550 °C in 1 × 10⁻⁶ Torr of pure oxygen (99.9995%). The films having c-axis orientation were grown with a thickness ranging from 28 to 55 nm. The thickness was precisely determined from x-ray diffraction analysis. The substrate SCAM has hexagonal lattice constants $a = 3.246 \text{ \AA}$ and $c = 25.195 \text{ \AA}$ having an

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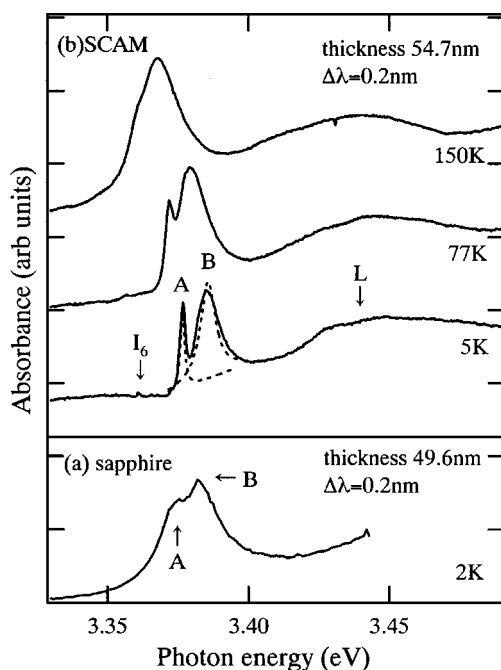


FIG. 1. (a) Temperature variation of absorption spectra in ZnO on an SCAM substrate. Measured temperatures are shown. “ I_6 ” with an arrow is the resonance energy position of an exciton bound to a neutral donor. Dotted curves correspond to the fitted results based on a double Lorentzian. (b) Spectrum of a ZnO epilayer on a sapphire substrate.

in-plane lattice mismatch as small as 0.09% for that of ZnO. The sample was kept in a cryostat for the temperature-dependent measurements. Reflection and transmission measurements were carried out using a xenon arc lamp as a light-emitting source and was monitored using a 0.3 m monochromator with a charge coupled device detector. The spectral resolution was approximately 0.2 nm, and a higher-resolution setup was used for photoluminescence (PL) measurements. The spectral resolution was less than 0.03 nm. The PL was excited by a cw He–Cd laser (325 nm).

Figure 1(a) shows temperature dependence of the absorption spectra in a ZnO epilayer on the SCAM substrate with a thickness of 54.7 nm, whereas Fig. 1(b) shows the absorption in ZnO on a sapphire substrate. The measured bath temperatures are shown in Fig. 1. The datum of Fig. 1(b) was taken from Refs. 3 and 11. Correction was made for reflection loss at the crystal surface. Dotted curves correspond to the fitted results, which will be explained later. In the exciton resonance region, four absorption bands, labeled I_6 , A, B, and L, could be observed at low temperatures (5–110 K), respectively. The resonance energies were estimated to be 3.3608 eV (368.8 nm), 3.377 eV (367.0 nm), 3.384 eV (366.3 nm), and 3.45 eV (359 nm), respectively at 5 K. The difference between the positions of the excitons in the epitaxial ZnO films and in bulk crystals is considered to be within the experimental error limited by the spectral resolution. These peaks were due to excitons bound to neutral donors (I_6),¹² A and B free excitons,¹² and exciton–LO phonon complex transitions,¹² respectively, by comparing the energy positions with literature values for bulk. On the other hand, it is difficult for a ZnO on sapphire to distinguish these two peaks (A and B) because they are close in energy and because of the large nonradiative damping constant of excitons. Although it is no longer possible to separate these two

bands above 150 K, a well-resolved exciton peak certainly appeared even at RT (not shown in Fig. 1). This is very similar to the spectrum for sapphire shown in Ref. 3. Good quality of this lattice-matching layer was also confirmed by temperature-dependent PL measurements. One dominant peak with a bound excitonic origin (same position in the case of the I_6 absorption band) was observed at 10 K, and deep-level PL was negligible compared with the intensity of I_6 . Furthermore, the FWHM of the PL band was equal to 0.8 meV or less. The width in ZnO on sapphire substrates is six times broader than that in ZnO/SCAM.

Observation of A and B exciton splitting in a ZnO epilayer on a sapphire substrate has been insisted previously in Ref. 13. The difference between the energetic positions in both absorption bands has been estimated to be comparable with the exciton binding energy, which was thought to be due to strain between a crystal and a substrate. Their assignment, however, is considered to be incorrect because the enhancement on the splitting energy due to the strain must not be so large. If we consider the thickness adopted in our experiments, a fine structure of size quantization where equidistant peaks (several meV) appear in the A exciton resonance region can be expected; however, we have not confirmed the existence of such peaks. Possible reasons for this may be that the spectral resolution is not sufficient, that the nonradiative damping constant of an A exciton is large, or that the broader B exciton band, whose tail overlaps the A band, disturbs the observation.

The energy difference between the A and L bands coincides with the LO phonon energy of 72 meV. In the case of ZnO, the selection rules for optical transitions are such that the A and B excitons should have a large oscillator strength for $E \perp c$ polarization and that the C exciton should have a large strength for $E \parallel c$ polarization. Since the sample is c-axis oriented, the oscillator strength of the C exciton must be small compared with that of the A and B excitons. Therefore, a more plausible assignment of the L band is indirect in the exciton–phonon transition, as it was done in a previous study.¹⁴

We have tried to fit the data in the A and B exciton resonance region with a double Lorentzian.¹⁵ The background was subtracted empirically.¹⁶ The relevant fitted results are shown in Fig. 1(b) with dashed curves. The fitting is in fairly good agreement with the experimental data to the extent that the width or area could be estimated and discussed separately for both exciton bands. The oscillator strength of the B exciton is six times larger than that of the A exciton at 5 K. Therefore, we estimated the FWHMs and plotted them against the bath temperature in Fig. 2 for A and B excitons, respectively. Squares correspond to the peak positions. Circles correspond to FWHM. A shift in the exciton energy as a function of temperature results essentially from a band-gap shift (based on the assumptions that exciton binding energy is temperature independent). As is well known, this derives from both thermal expansion and exciton–phonon interaction. The corresponding temperature dependence from both the mechanisms are very similar, and all the phonons, in principle, contribute to the shift. The overall contribution to the shift can be reproduced by Einstein approximation using the effective phonon energy $\hbar\bar{\omega}$, and in

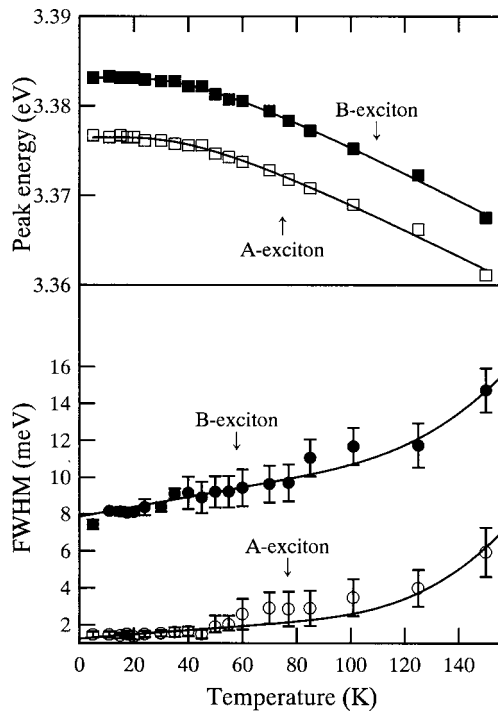


FIG. 2. Width (FWHM, circles) and peak energy (squares) of A and B exciton absorption bands plotted against temperature. Closed circles and squares correspond to the data of the A excitons, while the open ones correspond to those of the B excitons. The solid curves represent the fitting results based on Eqs. (1)–(2).

this case, the variation of exciton energy with temperature is given by

$$E(T) = E(0) - \lambda / [\exp(\hbar\bar{\omega}/k_B T) - 1], \quad (1)$$

where $E(0)$ is an exciton energy at $T=0$ K, and λ is a proportional coefficient. Estimated $\hbar\bar{\omega}$ (11.44 meV) approximately corresponds to the maximum energy of a low-frequency group of ZnO bulk phonons (12 meV). Table I shows λ and $\hbar\bar{\omega}$ for A and B excitons in ZnO. Data for a GaN homoepitaxial film¹⁷ as well as a ZnSe bulk crystal¹⁸ are listed in Table I for comparison.

The temperature dependences of FWHMs could be interpreted as a broadening due to the exciton–phonon scattering. We did not consider the piezoelectric contribution because the exciton is an electrically neutral substance. Interaction with LO phonons is dominant at a temperature higher than ≈ 100 K. The data could be fitted by the following expression. The equation for FWHM (Γ) is

$$\Gamma(T) = \Gamma_0 + \gamma_{ph} T + \Gamma_{LO} / [\exp(\hbar\omega_{LO}/k_B T) - 1], \quad (2)$$

where $\hbar\omega_{LO} = 72$ meV is the energy of a LO phonon, Γ_0 is the zero temperature broadening parameter, γ_{ph} is the coupling strength of an exciton–acoustic phonon interaction and Γ_{LO} is a parameter describing exciton–LO–phonon interaction. It was found that a reasonably good fit is obtained, and the results are summarized in Table I. The exciton–acoustic–phonon coupling strength was similar to values reported for other semiconductors, whereas that of exciton–LO–phonon coupling was outstandingly large. This is probably due to the high Fröhlich constant and the LO phonon energy of ZnO.

TABLE I. λ is the proportional coefficient, $\hbar\bar{\omega}$ is the effective phonon energy, γ_{ph} is the exciton–acoustic–phonon coupling strength, and Γ_{LO} is that of exciton–LO phonon. The former two parameters are deduced from Eq. (1), whereas the latter two are deduced from Eq. (2).

Material	λ (meV)	$\hbar\bar{\omega}$ (meV)	γ_{ph} (μ eV/K)	Γ_{LO} (meV)
ZnO (A)	20.9	11.44	11.3 ± 1.3	876.1 ± 113.7
ZnO (B)	11.48	21.8	26.5 ± 2.1	783.3 ± 50.5
GaN ^a	121	27.3	15.3	208
ZnSe ^b	32.1	9.9	64.2	126

^aFrom Ref. 17.

^bFrom Ref. 18.

In summary, undoped ZnO epilayers on SCAM substrates grown with L-MBE have shown a clear split by 7 or 8 meV for A and B excitons in the absorption spectra, a phenomenon that has not been observed so far for that on sapphire because of the high damping rate due to poor crystallinities. The use of lattice-matched SCAM substrates greatly improved the crystalline quality as well as optical (excitonic) properties of epitaxial ZnO layers. Such an improvement is favorable from the viewpoint of expectation of a reduction in the pumping threshold for laser action induced by the sharpened width of exciton energy states. Furthermore, coupling strengths of the exciton–acoustic–phonon and the exciton–LO phonon in ZnO were estimated from the temperature dependence of the absorption spectra.

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