

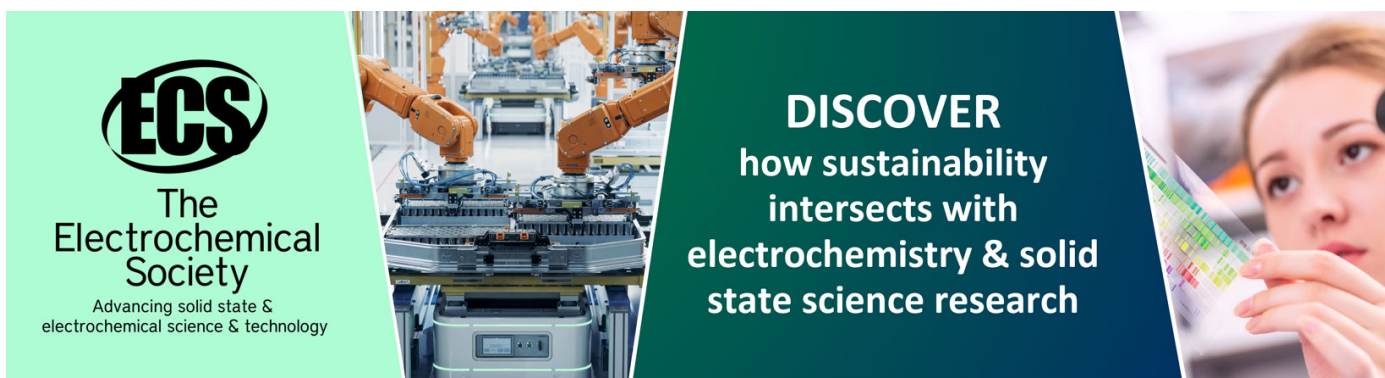
Exciton–polariton spectra and limiting factors for the room-temperature photoluminescence efficiency in ZnO

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Exciton–polariton spectra and limiting factors for the room-temperature photoluminescence efficiency in ZnO

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Abstract

Static and dynamic responses of excitons in state-of-the-art bulk and epitaxial ZnO are reviewed to support the possible realization of polariton lasers, which are coherent and monochromatic light sources due to Bose condensation of exciton–polaritons in semiconductor microcavities (MCs). To grasp the current problems and to pave the way for obtaining ZnO epilayers of improved quality, the following four principal subjects are treated: (i) polarized optical reflectance (OR), photorefectance (PR) and photoluminescence (PL) spectra of the bulk and epitaxial ZnO were recorded at 8 K. Energies of PR resonances corresponded to those of upper and lower exciton–polariton branches, where A-, B- and C-excitons couple simultaneously to an electromagnetic wave. PL peaks due to the corresponding polariton branches were observed. Longitudinal–transverse splittings (ω_{LT}) of the corresponding excitons were 1.5, 11.1 and 13.1 meV, respectively. The latter two values are more than two orders of magnitude greater than that of GaAs being 0.08 meV. (ii) Using these values and material parameters, corresponding vacuum-field Rabi splitting of exciton–polaritons coupled to a model MC mode was calculated to be 191 meV, which is the highest value ever reported for semiconductor MCs and satisfies the requirements to observe the strong exciton–light coupling regime necessary for polariton lasing above room temperature. (iii) Polarized OR and PR spectra of an out-plane nonpolar (1 1 $\bar{2}$ 0) ZnO epilayer grown by laser-assisted molecular beam epitaxy (L-MBE) were measured, since ZnO quantum wells (QWs) grown in nonpolar orientations are expected to show higher emission efficiencies due to the elimination of spontaneous and piezoelectric polarization fields normal to the QW plane. They exhibited in-plane anisotropic exciton resonances according to the

polarization selection rules for anisotropically-strained wurzite material. (iv) Impacts of point defects on the nonradiative processes in L-MBE ZnO were studied using time-resolved PL making a connection with the results of positron annihilation measurement. Free excitonic PL intensity at room temperature naturally increased with the increase in nonradiative lifetime (τ_{nr}). The value of τ_{nr} increased and density or size of Zn vacancies (V_{Zn}) decreased with increasing growth temperature (T_g) in heteroepitaxial films grown on a ScAlMgO₄ substrate, and the use of homoepitaxial substrates further reduced V_{Zn} density. The value of τ_{nr} was shown to increase with the decrease in gross density of positively and negatively charged and neutral point defects including complexes rather than with the decrease in V_{Zn} density. The results indicate that the nonradiative recombination process is governed not by single point defects, but by certain defects introduced with the incorporation of V_{Zn} , such as V_{Zn} -defect complexes. As a result of defect elimination by growing the films at high T_g followed by subsequent post-growth *in situ* annealing, combined with the use of high-temperature-annealed ZnO self-buffer layer, a record long τ_{nr} for spontaneous emission of 3.8 ns was obtained at room temperature. By using progressively improving epitaxial growth methods, the polariton laser effect is expected to be observed at room temperature in the near future.

1. Introduction

ZnO and related alloys are attracting attention, since they are excellent candidates for use in visible and ultraviolet (UV) light emitters, transparent field-effect transistors, sensors and piezoelectric devices as well as transparent conducting oxides: ZnO has a large exciton binding energy (59 meV) [1] and a large bandgap (3.4 eV) comparable to that of GaN. Rich excitonic features in ZnO have been investigated over 40 years. In 1960, Thomas [2] and Hopfield [3] assigned the sequence of three separate *p*-like valence bands in the order, Γ_{7v}^u , Γ_{9v} and Γ_{7v}^l with increasing transition energy to the *s*-like Γ_{7c} conduction band. Excitons related to the respective valence bands are referred to as A-, B- and C-excitons, respectively. In contrast, Reynolds *et al* [4] have assigned the ordering as A- Γ_{9v} , B- Γ_{7v}^u and C- Γ_{7v}^l by means of polarized optical reflectance (OR) and magnetoluminescence measurements. Gil [5] has supported the latter assignment by calculating the oscillator strengths of the respective excitons taking the short-range electron-hole exchange interaction into account: the band assignment is still in debate. Nevertheless, both models predict that A- and B-transitions are allowed for the light polarization *E* perpendicular to the optic (*c*-) axis ($E \perp c$), where *E* is the electric field component, and the C-transition is essentially allowed for the light polarization *E* parallel to the *c*-axis ($E // c$). The resonance energies of the ground-state A-, B- and C-excitons in strain-free bulk crystals have been determined by means of OR measurements [2, 4, 6] to be approximately $E_A = 3.377$, $E_B = 3.386$ and $E_C = 3.4215$ eV at 4.2 K.

Since excitons in ZnO are stable at room temperature [1], ZnO is of considerable interest for realization of cavity-coupled polariton lasers [7] operated at room temperature [8], in which the coherent light amplification is induced due to Bose condensation of exciton-polaritons [9]; the operation principles being different from usual semiconductor lasers based on the population inversion of electron-hole plasma.

Bulk and surface exciton-polaritons in ZnO single crystals, where A-, B- and C-excitons couple simultaneously to an electromagnetic wave, have been investigated by Hümmer and Gebhardt [10] and Lagois [11] using angular-resolved OR and the attenuated total reflection method. They have fitted the spectra theoretically taking the *exciton dead layer* into account to determine the energies of respective upper and lower polariton branches (UPB and LPB, respectively). They have obtained the longitudinal-transverse splitting (ω_{LT}), which is the energy difference between the longitudinal and transverse excitons (ω_L and ω_T , respectively), of the B-exciton to be 11 meV, which was more than two orders of magnitude greater than that of GaAs being 0.08 meV. Since ω_{LT} is proportional to the oscillator strength of excitons and represents the stability of exciton-polaritons, the value predicts gigantic vacuum-field Rabi splitting (Ω_{Rabi}) of ZnO microcavity (MC) polaritons [8].

To fabricate light-emitting diodes (LEDs), laser diodes (LDs) and polariton lasers with ultrathin quantum structures of abrupt interfaces, research on the epitaxial formation of ZnO has been accelerated using a variety of methods such as laser-assisted molecular beam epitaxy (L-MBE) [12–16], molecular beam epitaxy (MBE) [17–20], chemical vapour deposition [21], metal organic vapour phase epitaxy [22] and helicon-wave-excited plasma sputtering epitaxy [23]. As a result of the research progress, the clear indication, that the excitonic effect is obvious even at temperatures higher than 300 K, has been given by the observation of stimulated emissions due to the strong Coulomb interaction (excitonic gain) from ZnO epilayers [12–14, 18]. Moreover, attempts to grow p-type ZnO by N-doping have been carried out [16, 20, 21] and photoluminescence (PL) peaks due to N acceptors have been investigated [20, 24, 25]. Eventually, Tsukazaki *et al* [26] realized the reproducible growth of N-doped p-type ZnO by the repeated-temperature-modulation L-MBE method, and observed UV and visible electroluminescence from a p-n junction LED grown on high-temperature-annealed ZnO self-buffer layers [27] on nearly lattice-matched (0.09% in-plane)

(0001) ScMgAlO₄ (SCAM) substrates. However, undoped ZnO usually shows n-type conductivity with high residual free electron concentration. The source of free electrons has been attributed to positively charged point defects such as Zn interstitials (Zn_i) and O vacancies (V_O). On the other hand, the role of neutral and negatively charged defects [28] has not been clarified yet. Since the quantum efficiency (η) of exciton emissions is determined by radiative and nonradiative recombination lifetimes (τ_r and τ_{nr} , respectively) in a form $\eta = 1/(1 + \tau_r/\tau_{nr})$, it is an important task to find the origin of nonradiative recombination centres correlating τ_{nr} and defect species, in order to give a way of eliminating those defects to improve η . To comply, a combination of analytical methods of time-resolved PL (TRPL) and positron annihilation methods is effective [29, 30].

Positron annihilation [31–36] is an established technique for detecting negatively charged (or neutral) vacancy defects in semiconductors. An implanted positron annihilates with an electron and emits two 511 keV γ -rays, which are broadened due to the momentum component of the annihilating positron–electron pair. Because the momentum distribution of electrons in such defects differs from that in defect-free regions, the defects can be detected by measuring the Doppler broadening spectra of annihilation radiation. The resulting change in the γ -ray spectra is characterized by S and W parameters [31–35], the former mainly reflects the fraction of annihilating positron–electron pairs of small momentum distribution, and the latter represents the fraction of the pairs of large momentum distribution. Since Zn vacancies (V_{Zn}) and their complexes, which have negative charges forming acceptor-type defects in n-type ZnO [35], are the most probable candidates of positron trapping centres in ZnO, S and W can be used as a measure of the density/size of V_{Zn}. For multilayer structures, characteristic S and positron diffusion length (L_d) in each layer can be determined by using a monoenergetic positron beam [32], by which the mean implantation depth can be adjusted. The analysis [32–36] involves solving the diffusion equation of positrons using the initial implantation profile as a function of positron acceleration energy E . The value of L_d can be used as a measure of gross density of positron trapping centres (V_{Zn} and V_{Zn}-complexes) plus positron scattering centres (positively charged V_O, Zn_i, O interstitials O_i and complexes), because both of them shorten L_d [29, 35].

Recently, wurzite AlInGaN grown in out-plane nonpolar orientations such as (1 $\bar{1}$ 00) and (11 $\bar{2}$ 0) faces are attracting great attention [37, 38], since the strained quantum wells (QWs) formed on nonpolar faces do not suffer from the quantum-confined Stark effect (QCSE) due to the polarization fields [39], which severely reduce η in polar (0001) QWs. However, the growth of ZnO in nonpolar orientations is still immature, and little is known about the anisotropic optical transitions in nonpolar ZnO epilayers [40, 41].

In this paper, static and dynamic responses of excitons in the bulk and epitaxial ZnO are reviewed to support the fabrication of room-temperature polariton lasers based on ZnO MCs. The following four important topics are treated to view current issues and to indicate a way of improving epilayer quality: (i) low temperature OR and photorefectance (PR) spectra of (0001) ZnO epilayers exhibited distinct exciton–polariton features [41–43] showing that A- and B-exciton resonances dominate the spectra according to the

polarization selection rules [1–5] similar to the case for the optical absorption (OA) spectra [44, 45]. Low-temperature PL spectra of the epilayers grown on SCAM as well as the bulk ZnO single crystal exhibited corresponding excitonic polariton emissions [6, 41, 43]; values of ω_{LT} for A-, B- and C-exciton polariton branches were obtained to be 1.5, 11.1 and 13.1 meV, respectively. (ii) Using these values and material parameters, Ω_{Rabi} of the model ZnO MC polaritons [8] was calculated to be 191 meV, which is the highest value ever reported for semiconductor MCs, and the value satisfies the requirements to observe the strong exciton–light coupling regime necessary for polariton lasing above room temperature. (iii) Polarized optical spectra of an out-plane nonpolar (11 $\bar{2}$ 0) ZnO epilayer exhibited in-plane anisotropic exciton resonances according to the polarization selection rules for anisotropically strained wurzite material. (iv) PL lifetimes (τ_{PL}) of the films at room temperature were measured by TRPL making a connection with the results of positron annihilation measurement, to correlate the nonradiative recombination centres and point defects. The nonradiative recombination process was found to be governed not by single point defects, but by certain defects introduced with the incorporation of V_{Zn} such as V_{Zn}-defect complexes. Finally, as a result of defect management by growing the films at high growth temperature (T_g) followed by subsequent post-growth *in situ* annealing, combined with the use of high-temperature-annealed ZnO self-buffer layers, a record long τ_{nr} for the spontaneous emission of 3.8 ns was obtained at room temperature.

2. Experimental details

Samples investigated were: (i) undoped bulk ZnO crystal grown by the seeded chemical vapour deposition method [4, 6, 20, 35, 46], (ii) an approximately 1 μ m-thick undoped (000 $\bar{1}$) ZnO epilayer grown by radical-source (RS-) MBE on (11 $\bar{2}$ 0) Al₂O₃ [19, 43], in which the a -axis of the epilayer was locked uniaxially and (iii) 50 nm to 1 μ m-thick undoped ZnO epilayers grown by combinatorial L-MBE [26, 27, 30, 35, 41] ablating a ZnO single crystal target [46] using a KrF excimer laser. The L-MBE samples were heteroepitaxial (000 $\bar{1}$) ZnO on SCAM substrates, homoepitaxial (000 $\bar{1}$) ZnO on a ZnO single crystal or on the (000 $\bar{1}$) ZnO high-temperature-annealed self-buffer structures prepared on SCAM [27], and a (0001) ZnO on a ZnO single crystal. Typical T_g was between 550 °C and 1050 °C. Some of the samples grown on the self-buffer were annealed during the post-growth cooling under controlled O₂ ambient pressures. (iv) A nonpolar (11 $\bar{2}$ 0) ZnO film on (10 $\bar{1}$ 2) Al₂O₃ was also grown by L-MBE at 650 °C [41], in order to study the effects of anisotropic strains on the band structures. Its in-plane orientation was [0001] ZnO//[0 $\bar{1}$ 11] Al₂O₃, and the value of full-width at half-maximum (FWHM) of the ZnO (11 $\bar{2}$ 0) x-ray rocking curve (XRC) was as large as 1100 arcsec. Note that those of ZnO (0002) XRC of polar films were comparable to those of the substrates [27].

OR, PR, PL and TRPL measurements were carried out as a function of temperature. For OR and PR measurements, a white light from a 300 W Xe lamp was focused on a desired face. For the polarized OR, PR and PL measurements on the bulk ZnO single crystal, both a well-developed (000 $\bar{1}$) face

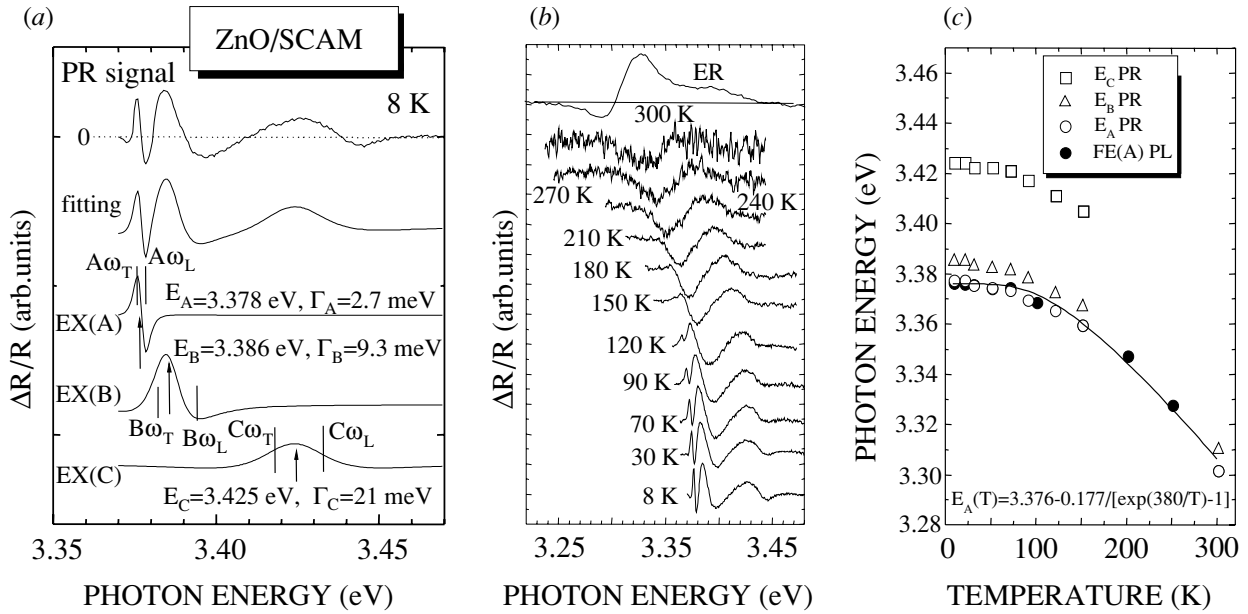


Figure 1. (a) PR spectrum at 8 K of a 50 nm-thick (000 $\bar{1}$) ZnO epilayer on the SCAM substrate (upper trace) after [42]. The second trace shows the fitting result using equation (1). The bottom three traces labelled EX(A), EX(B) and EX(C) represent A-, B- and C-exciton components, respectively, in which the resonance energies E_α ($\alpha = A, B$ and C) are shown by the arrows. The vertical lines labelled $\alpha\omega_L$ and $\alpha\omega_T$ show the energies of longitudinal and transverse α -exciton in the strain-free ZnO, respectively, which are taken from [10]. (b) PR spectra and (c) excitonic transition energies as a function of temperature.

and a cleaved $\{11\bar{2}0\}$ face were examined. The incidence angle was smaller than 15° , and that for the PL collection was 0° . Reflected light and PL were polarized using a Glan–Thompson prism polarizer, and were dispersed by a 67 cm focal-length grating monochromator after passing through a depolarizer. PR and PL spectra were measured using the 325.0 nm line of a cw He–Cd laser as the excitation source. PLE spectra were recorded by monitoring the lower energy tail of the near-band-edge bound exciton emissions (3.355 eV) using a monochromatic light from a 300 W Xe lamp. The spectral resolution was 0.12 nm (nearly 1 meV at the wavelength of 370 nm) for PR measurement and 0.006 nm (nearly 70 μ eV at the wavelength of 370 nm) for OR and PL measurements. Details of the PR, PL and OR measurement system will be found elsewhere [47]. TRPL measurements were carried out at 293 K using a frequency-doubled mode-locked Ti:Al₂O₃ laser (362.5 nm, 3 mW, ~ 80 fs) and the signal was collected using a standard streak-camera acquisition system. The monoenergetic positron beam line [34, 35] was used to determine S and W parameters as a function of E , and L_d was calculated by the fitting using the positron diffusion equation based on the analysis using the algorithm named VEPFIT [36]. The analytical procedures used in this study were similar to those described in [34, 35].

3. Results and discussion

3.1. PR spectra of a ZnO film grown by L-MBE

In order to determine exciton resonance energies, the PR method is known to be useful since it is a contactless form of the electroreflectance (ER) method. The signal is obtained as the change in the reflectivity (ΔR) due to the external

light (field) modulation divided by the cw reflectivity (R), and therefore $\Delta R/R$ is proportional to the derivatives of the dielectric function [48]. However, there have been no reported results on the PR spectrum of ZnO until 2002 [42], though ER spectra have been investigated intensively from the 1960s [48, 49]. PR spectrum at 8 K of a 50 nm-thick (000 $\bar{1}$) ZnO epilayer grown by L-MBE on the SCAM substrate is shown by the top trace in figure 1(a). The spectrum exhibited three distinct resonance structures, and the spectrum was analysed by the low-field electroreflectance lineshape function [50]

$$\frac{\Delta R}{R} = \text{Re} \left\{ \sum_{j=1}^p C_j e^{i\theta_j} [\hbar\omega - E(j) + i\Gamma_j]^{-m_j} \right\}, \quad (1)$$

where $p = 3$ is the number of the spectral function to be fitted and C_j , θ_j , $E(j)$ and Γ_j are the amplitude, phase, exciton resonance energy and broadening parameter of the j th feature, respectively. m_j is a parameter that depends on the critical point type. In this study, the value $m_j = 2$ (exciton transition) [50] gave the best fit to the experimental data. The fitting result is shown by the second trace in figure 1(a). The bottom three traces labelled EX(A), EX(B) and EX(C) represent A-, B- and C-exciton components, respectively. It should be noted that C-exciton resonance was also observed in the spectrum due to the finite incidence angle of the light. Transition energies were thus obtained to be $E_A = 3.378$ eV, $E_B = 3.386$ eV and $E_C = 3.425$ eV and the energy positions are indicated by arrows. It should be noted that Γ_B and Γ_C were 9.3 and 21 meV, respectively, which were more than three times larger than Γ_A (2.7 meV). One of the plausible explanations of this was an inhomogeneous distribution of the residual strain, since E_C shifts more rapidly than E_B which itself shifts more rapidly than E_A under strain [51]. However, if the whole Γ_B (9.3 meV) was attributed to inhomogeneous distribution of strain, Γ_A and

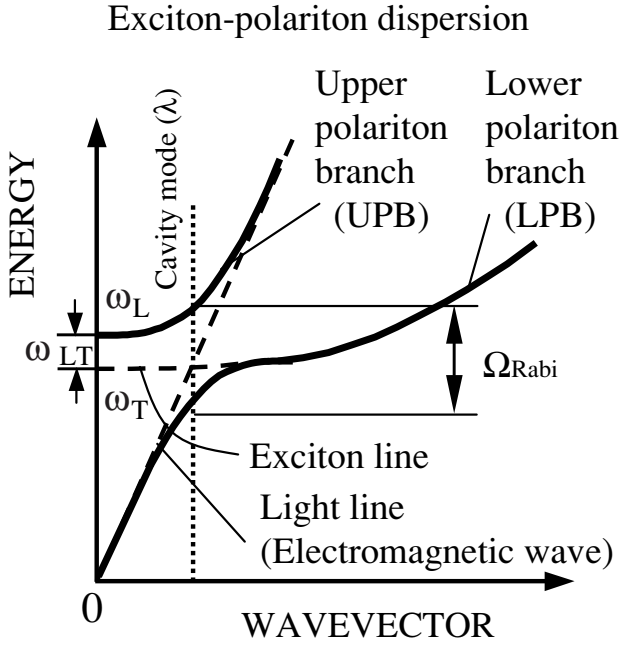


Figure 2. Dispersion relation of exciton-polaritons. Dashed lines show the dispersion of isolated excitons and light in the material. Longitudinal-transverse splitting of the exciton ω_{LT} , which is the energy difference between ω_L and ω_T at wavevector $k = 0$, represents the stability of exciton-polaritons. If k is locked at the dotted line, the energy difference between UPB and LPB (vacuum field Rabi splitting Ω_{Rabi}) is also locked to have a larger value than the initial ω_{LT} , indicating that the coupling between the exciton and light became effectively strong.

Γ_C are to be 2 and 12 meV, respectively, according to Gil *et al* [51]. Although this effect should not be disregarded, the Γ_C value was too large to be accounted for only by the strain inhomogeneity; the broadness of B- and C-transitions was explained considering the contribution by exciton-polaritons, as follows. Note that the dispersion relation of exciton-polaritons is depicted in figure 2. According to Hümmer and Gebhardt [10], ω_{LT} for A-, B- and C-excitons are approximately 2, 11 and 16 meV, respectively. The Γ values obtained in this work nearly agreed with them [10]; ω_L and ω_T for the respective excitonic polaritons in strain-free ZnO [11] are shown by vertical lines in figure 1(a). Since the epilayer thickness was 50 nm, which was thinner than the exciton resonance wavelength λ in the material and is not an integer multiple of $\lambda/2$, it may be difficult to pin exciton-polaritons. However, the precursor of polariton formation is considered to be found by the broadening of the respective exciton structures. Note that the large ω_{LT} for B- and C-excitons is indicative of large oscillator strength, since $\omega_{LT} = f_{\perp} \omega_0 / \epsilon_{0\perp}$, where $f_{\perp}$ and $\epsilon_{0\perp}$ are the oscillator strength and the dielectric tensor component in the plane normal to the optical axis, respectively, and ω_0 is the exciton resonance energy. Indeed, $f_{\perp}$ of B- and C-excitons have been reported to be more than four times that of the A-exciton [2].

PR and ER spectra are shown as a function of temperature in figure 1(b). The PR signal intensity due to A-transition decreased rapidly with the increase in temperature, and the spectra were dominated by B- (and C-) transitions at higher temperatures. The result was consistent with larger $f_{\perp}$ of B-

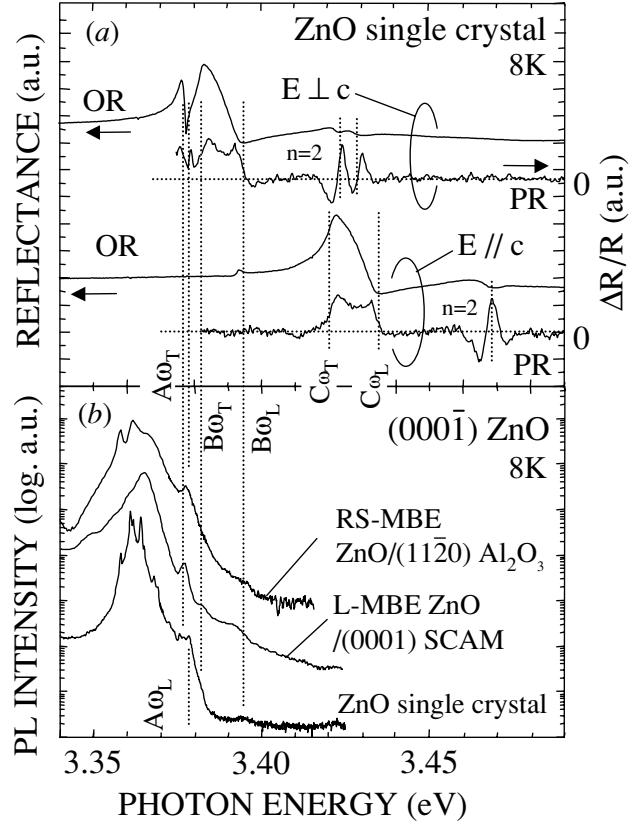


Figure 3. (a) OR and PR spectra at 8 K of a high-quality ZnO single crystal measured under the light polarization $E \perp c$ and $E // c$, where E is the electric field component and c is the optic axis [6]. $A\omega_T$, $A\omega_L$, $B\omega_T$, $B\omega_L$, $C\omega_T$ and $C\omega_L$ are the energies of transverse and longitudinal A-, B- and C-excitons, respectively. A ($n = 2$) and B ($n = 2$) are resonances due to the first excited states of A- and B-excitons, respectively. (b) PL spectra of the ZnO bulk single crystal [6] and approximately 1 μm -thick (0001) ZnO epilayers grown by RS-MBE on (11-20) Al_2O_3 [43] and L-MBE on SCAM substrates [41].

(and C-) excitons. The dependence of E_A and $FE(A)$, the latter being the free A-exciton emission peak energy, on temperature can be fitted by Bose-Einstein statistics, as shown by the solid curve in figure 1(c) giving an Einstein characteristic temperature Θ_E of 380 K (33 meV or 268 cm^{-1}). This value is in good agreement with the energy maximum of the low-energy group of bulk phonon density of states (8 THz = 33 meV or 380 K) [52].

3.2. Exciton-polaritons in ZnO

Polarized OR and PR spectra and PL spectra at 8 K of a high-quality ZnO single crystal [43] are shown in figures 3(a) and (b), respectively [6]. For $E \perp c$, the OR spectrum exhibited strong anomalies around 3.38 and 3.39 eV, which are due to the ground state ($n = 1$) A- and B-excitons, respectively. In addition, remarkable anomalies were observed at around 3.42 and 3.43 eV, which were assigned to the first excited states ($n = 2$) of A- and B-excitons, respectively. In the figure, the positions of ω_T and ω_L for A-, B- and C-excitonic polaritons [11] are drawn by vertical dotted lines (labelled $A\omega_T$, $A\omega_L$, $B\omega_T$, $B\omega_L$, $C\omega_T$ and $C\omega_L$). Obviously, the PR spectrum

Table 1. Exciton–polariton parameters in ZnO single crystal determined by the OR measurements [6] and those in free-standing GaN [53, 54] prepared by the lateral epitaxial overgrowth technique and subsequent substrate polishing [62].

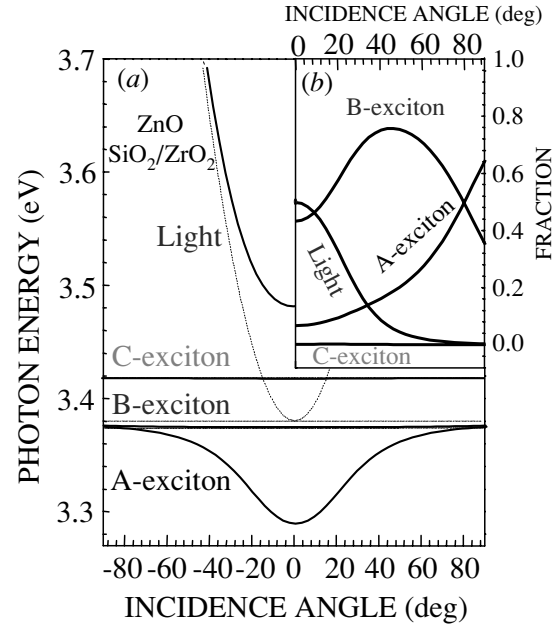
Exciton	Polarization	ZnO (meV) [6]					GaN (meV) [54]		
		$n = 1$			$n = 2$	E_{ex}	GaN (meV) [54]		
		ω_{T}	ω_{L}	ω_{LT}			ω_{T}	ω_{LT}	E_{ex}
A (Γ_9)	$\perp$	3376.8	3378.3	1.5	3423.1	60	3479.1	1.34	23.44
B (Γ_7)	$\perp(//)$	3383.0	3394.1	11.1	3429.0	53	3484.4	1.17	23.6
C (Γ_7)	$//(\perp)$	3348.4	3435.3	13.9	3467.9	49	3502.7	0.27	(20.3)

exhibited fairly noisy but fine structures at those energies, implying a formation of exciton–polaritons. The PR signal $\Delta R/R$ given by equation (1) is deduced as [48–50]

$$\frac{\Delta R}{R} = \text{Re} \left\{ \frac{2n_a}{n(\varepsilon - \varepsilon_a)} \right\} = \text{Re}\{(\alpha - i\beta)\Delta\varepsilon\} = \alpha\Delta\varepsilon_1 + \beta\Delta\varepsilon_2, \quad (2)$$

where $n^2 = \varepsilon$, $n_a^2 = \varepsilon_a$, n_a is the real part of the refractive index, $\Delta\varepsilon = \Delta\varepsilon_1 + i\Delta\varepsilon_2$ is the perturbation-induced change in the dielectric function ε , and α and β are the Seraphin coefficients. Equation (2) implies that the signal $\Delta R/R$ is purely sensitive to $\Delta\varepsilon$; i.e. the PR method monitors exciton resonances in wide bandgap materials. Therefore, observation of exciton–polaritons by the PR method [6, 42, 43, 47, 53, 54] is reasonable since they represent a coupled state between an electromagnetic wave and excitons. The value of ω_{LT} for the B-excitonic polariton was confirmed to be as large as 11.1 meV, implying the large oscillator strength. The energies obtained from figure 3 are summarized in table 1, together with the data obtained for GaN [54]. For $E//c$, the OR spectrum exhibited a strong and a weak anomaly around 3.43 and 3.47 eV, which are due to $n = 1$ and $n = 2$ C-exciton resonances, respectively. As is the case with A- and B-excitons, the PR signal exhibited fine structures at ω_{T} and ω_{L} , giving the ω_{LT} of the C-exciton as large as 13.9 meV. From these values, the spin–orbit splitting and crystal field splitting were estimated by the quasi-cubic model [3] to be 14 and 48 meV, respectively.

PL spectra of the ZnO bulk single crystal [6] and approximately 1 μm -thick (000 $\bar{1}$) ZnO epilayers grown by RS-MBE on (11 $\bar{2}$ 0) Al_2O_3 [43] and L-MBE on SCAM [41] are shown in figure 3(b), where a logarithmic y-axis is used. Sharp PL lines between 3.355 and 3.372 eV observed in the bulk single crystal (bottom trace) have been assigned to a series of bound exciton complex recombination emissions. Detailed studies on these lines have been carried out by several researchers [4, 20, 25, 46]. In addition, the PL spectrum exhibited a weak but noticeable peak at 3.3941 eV and a shoulder at 3.3830 eV. They were assigned as being due to the emission of $B\omega_{\text{L}}$ and $B\omega_{\text{T}}$, respectively, since the energy agreed with those determined from the OR and PR spectra. Although the picture is not clear, PL peaks at 3.3783, 3.3765 and 3.3755 eV were found in the bottom spectrum [6]. They were essentially polarized to $E \perp c$ and were assigned to the emission of $A\omega_{\text{L}}$ and $A\omega_{\text{T}}$ and a bound exciton, respectively, judging from the energy positions [6]. Observation of these exciton–polariton emissions implies that the ZnO single crystal was of good quality. Since the exciton–polariton emissions were also found in the improved ZnO epilayers, as shown in figure 3(b), and the fabrication of p–n junction LEDs was

**Figure 4.** Eigenenergies of the ZnO cavity modes versus the incidence angle. Dotted lines indicate the positions of the unperturbed modes: ‘light’ indicates the light mode, and A-, B- and C-exciton indicate the A-, B- and C-exciton resonances in ZnO, respectively. The inset shows the percentage of the excitonic components and the photonic component in the eigen mode of the lowest cavity-polariton state versus the in-plane wave vector.

realized [26], epitaxial formation of ZnO-based MCs [8] is now considered to be possible.

The calculated exciton–polariton dispersion in the model MC described below is shown in figure 4(a). The calculation procedure was the same as that carried out in [8] except for eigenenergies of A-, B- and C-excitons and the cavity structure. The model MC considered herein consisted of the λ cavity of ZnO sandwiched between eight pairs of $\text{SiO}_2/\text{ZrO}_2$ and seven pairs of $\text{ZrO}_2/\text{SiO}_2$ dielectric distributed Bragg reflectors of quarter-wavelength layers in the bottom and top mirrors, respectively. SiO_2 was assumed as a substrate. The cavity photon mode was placed at 3.383 eV (366.5 nm in vacuum) at zero detuning from the B-exciton resonance, since the B-exciton has a large ω_{LT} of 11.1 meV and is polarized to $E \perp c$. Refractive indices of ZnO, SiO_2 and ZrO_2 at 366.5 nm were taken as 2 [8, 55], 1.48 [56] and 2.1 [57], respectively. The ZnO, SiO_2 and ZrO_2 layer thicknesses were 183.2, 61.9 and 44.7 nm, respectively. In figure 4, four branches arising from A-, B- and C-exciton resonances and the cavity light mode (denoted by ‘light’) are shown. Dotted thin lines indicate the positions of the corresponding unperturbed modes. Among

those, the lowest polariton branch is of the greatest interest for realization of polariton Bose condensation and lasing. The inset shows the percentage of the excitonic components and the photonic component in the eigen mode of the lowest cavity-coupled polariton state as a function of in-plane wave vector.

The important findings are the following. (I) Zero wavevector is locked by the cavity at which unperturbed B-exciton resonance and light line crossover (shown by the dotted line in figure 2), leading to an increase in Ω_{Rabi} up to 191 meV due to the enhanced coupling between B-exciton and light modes. This value is the highest value ever recorded for semiconductor MCs. The difference between the present value and that calculated by Zamfirescu *et al* (120 meV) [8] arose from the change in ω_{LT} values of excitons, presumably due to the experimental determination of the resonance energies. (II) The eigenfunction of the fundamental state at zero incidence angle has less than 50% of the photonic component (see the inset), which is essential for efficient polariton relaxation towards the ground state through scattering of the excitonic component with acoustic phonons, other excitons and free carriers introduced in the cavity. (III) The fundamental state has 40% B-excitonic character at zero incidence angle and it increases to 80% for the incidence angle of 40° . Results (II) and (III) mean that the B-excitonic character is strongly reflected to the lowest polariton branch denoted by ‘A-exciton’ in figure 4 [8], in which Bose condensation of polaritons is expected in a cavity polariton laser structure [9]. Using the values listed in table 1 and the polariton dispersion relation given in figure 4, the critical density of formation of Bose condensation of exciton–polaritons in the model MC was calculated as a function of temperature. As a result, a critical temperature of 610 K was given from the exciton dissociation energy, and allowable exciton density between $1 \times 10^{12} \text{ cm}^{-2}$ and $7 \times 10^{13} \text{ cm}^{-2}$ at 300 K was obtained due to the large electron–hole plasma density to screen excitons (Mott density for excitons). By using progressively improving epitaxial growth methods, the polariton laser effect due to Bose condensation will probably be observed at room temperature in the near future.

3.3. Excitons in nonpolar face ZnO

Polarized OR and PR spectra of an out-plane nonpolar (11 $\bar{2}$ 0) ZnO epilayer grown by L-MBE exhibited anisotropic exciton resonance structures [41] according to the polarization selection rules for anisotropically strained wurzite material [58], as follows. Polarized PR, OR and PL spectra of (11 $\bar{2}$ 0) ZnO measured at 8 K are shown in figure 5. The PR and OR spectra exhibited excitonic resonance structures at 3.402 eV

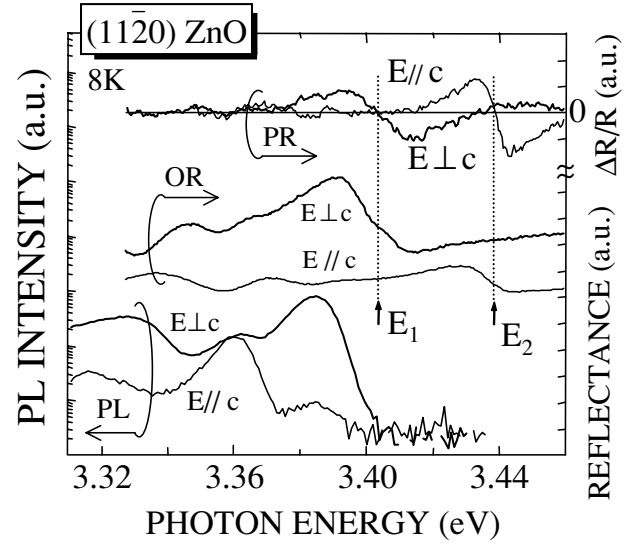


Figure 5. Polarized PR, OR and PL spectra at 8 K of the (11 $\bar{2}$ 0) ZnO epilayer grown on (10 $\bar{1}$ 2) Al₂O₃ grown by L-MBE at 650 °C [41]. E_1 and E_2 represent the energies of exciton transitions observed for $E_{\perp c}$ and $E_{\parallel c}$, respectively, in OR and PR spectra.

and 3.439 eV for $E_{\perp c}$ and $E_{\parallel c}$, respectively. These energies were higher than those of A- (or B-) and C-excitons in strain-free ZnO [1–6, 59]. The energy shift is due to anisotropic strains [58] caused by the lattice and thermal expansion mismatches. The strains are quantified by x-ray diffraction (XRD) measurements to be -0.41% , -0.19% and $+0.49\%$ along [11 $\bar{1}$ 0], [0001] and [11 $\bar{2}$ 0] directions, respectively, where minus and plus signs represent compressive and tensile, respectively. Since these anisotropic strains change the crystal symmetry from C_{6v} to C_{2v} , the labels A, B and C can no longer be used. Therefore, nomenclatures E_1 , E_2 and E_3 for the ground state of the three excitons are used, as Ghosh *et al* [58] have used to describe exciton structures in nonpolar (1 $\bar{1}$ 00) GaN. They have calculated the oscillator strengths and transition energies of excitons in anisotropically-strained GaN [58], which has C_{6v} symmetry and valence band ordering of A- Γ_9 , B- Γ_7 and C- Γ_7 . According to their calculation, E_1 , E_2 and E_3 excitons in our strained (11 $\bar{2}$ 0) ZnO are predominantly polarized to [1 $\bar{1}$ 00], [0001] and [11 $\bar{2}$ 0], respectively. Therefore, transition structures observed under $E_{\perp c}$ (3.402 eV) and $E_{\parallel c}$ (3.439 eV) are assigned to E_1 and E_2 transitions, respectively, as shown in table 2. The E_3 transition is not observed, since the [11 $\bar{2}$ 0] direction is normal to the surface. Consistent with the polarization selection rules for the E_1 transition, a near-band-edge PL peak at 3.384 eV in the

Table 2. Exciton parameters in anisotropically-strained (11 $\bar{2}$ 0) ZnO and nearly strain-free (0001) and (000 $\bar{1}$) ZnO epilayers at 8 K.

Strained (11 $\bar{2}$ 0) ZnO			Nearly strain-free (0001) and (000 $\bar{1}$) ZnO		
Exciton ^a	Polarization ^b	Energy(eV)	Exciton	Polarization	Energy (eV)
E_1	$E_{\parallel}[1\bar{1}00]$	3.402	A	$E_{\perp}[0001]$	3.377
E_2	$E_{\parallel}[0001]$	3.439	B	$E_{\perp}[0001]$	3.383(T), 3.393(L)
E_3	$E_{\parallel}[11\bar{2}0]$	Not allowed	C	$E_{\parallel}[0001]$	–

^a Notation according to [58].

^b Calculation according to [58].

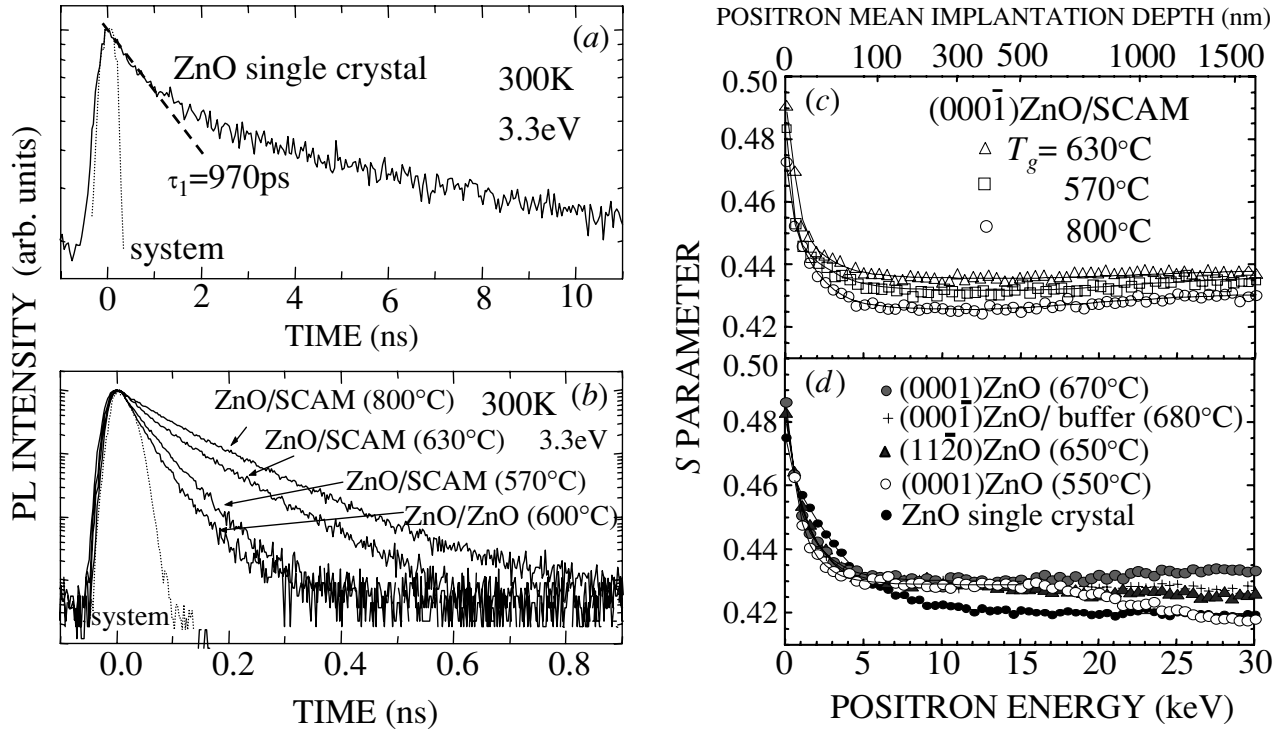


Figure 6. Representative TRPL signals of the near-band-edge emission at 3.3 eV for (a) the ZnO single crystal and (b) L-MBE films measured at 293 K. Doppler broadening S parameter of (c) heteroepitaxial (0001) ZnO layers on SCAM and (d) homoepitaxial {0001} ZnO films and heteroepitaxial nonpolar (1120) ZnO epilayer on (1012) Al_2O_3 as a function of incident positron energy E . The solid curves in (c) and (d) show the results of fitting the experimental data.

(1120) ZnO film is polarized to $E \perp c$ (parallel to $[1\bar{1}00]$). Because the peak energy is lower by 18 meV than the E_1 transition energy, the peak is tentatively assigned to the I_6 peak (3.36 eV in strain-free ZnO) [60], which has been assigned to the recombination of excitons bound to a neutral Al donor [59]. From the fact that state-of-the-art nearly strain-free (0001) and (0001) ZnO films grown by L-MBE exhibit free exciton emissions and exciton–polariton emissions [27, 41], as shown in figure 3, residual anisotropic and inhomogeneous strains in the (1120) ZnO film are considered to degrade the electronic quality to observe free excitons and simultaneously to cause the broadening of FWHM values of XRD and PL peaks. Therefore, a lattice and thermally-matched substrate is necessary to further improve the exciton spectra of the (1120) ZnO epilayers. Nevertheless, the observation of correct in-plane polarization of the exciton transitions is encouraging in designing (1120) or (1100) nonpolar face devices using epitaxial ZnO grown in nonpolar orientations, as is the case in AlInGaN materials [37, 38, 58, 61].

3.4. Exciton dynamics and point defects in ZnO epilayers

In order to improve the overall epilayer qualities for the realization of high η LEDs using p-type ZnO, it is an important task to figure out the origin of nonradiative recombination centres correlating τ_{nr} and defect species. To complete this purpose, a combination of analytical methods of TRPL and monoenergetic positron annihilation methods has been carried out [29, 30, 35, 41]. Representative TRPL signals of the near-band-edge emission at 3.3 eV, which has been assigned to the free exciton emission, for the ZnO single crystal and ZnO

epilayers grown by L-MBE on SCAM measured at 293 K are shown in figures 6(a) and (b), respectively [30]. The bulk ZnO exhibited a biexponential decay with long lifetimes of the order of 1 and 14 ns for the fast and slow components, respectively. Both of them represent nonradiative recombination lifetimes originating from two different nonradiative pathways. Note that the value 970 ps was comparable to that of GaN single crystal being 860 ps [29, 62], suggesting that the material contained a small number of nonradiative defects. On the other hand, the epilayers showed a single exponential decay with much shorter lifetimes. Because τ_{PL} at 293 K is, in general, dominated by τ_{nr} due to the activation of nonradiative defects, short τ_{PL} values for the epilayers suggested the presence of higher density nonradiative defects compared with the bulk crystal at that time [30, 41]. Nevertheless, nonradiative defect density in ZnO/SCAM was considered to be reduced by increasing T_g , because τ_{PL} increased with the increase in T_g , as shown in figure 6(b).

S parameter of heteroepitaxial (0001) ZnO layers on SCAM and that in homoepitaxial {0001} ZnO films and the nonpolar (1120) ZnO epilayer are shown as a function of incident positron energy E in figures 6(c) and (d), respectively [30, 35]. The mean implantation depth of positrons is shown in the upper horizontal axis. The increase in S at low E (≤ 0 keV) is due to the annihilation of positrons and positronium atoms at the surface, and the S values at high E (≥ 20 keV) include the information of the substrate. The constant S values for $E = 10$ –15 keV mean that most of the positrons annihilate in the films. Solid curves show the fitting results [35] of the positron diffusion equation. The fitting curves well reproduced the experimental data, and the values of S and L_d are shown

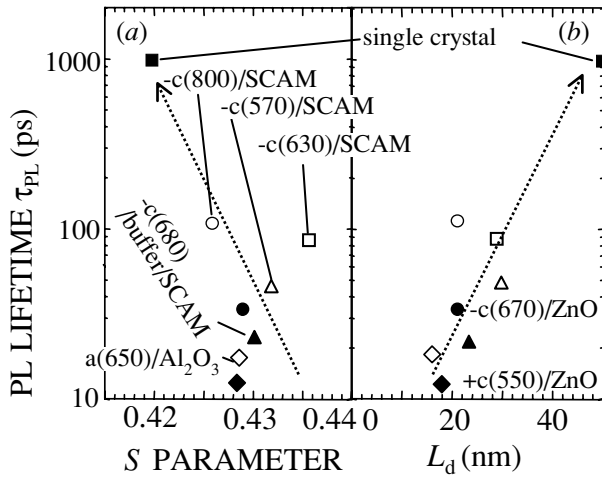


Figure 7. TRPL decay constants of the near-band-edge excitonic PL peak at 293 K, which in general determine the time-integrated intensity at room temperature, in the bulk, heteroepitaxial and homoepitaxial ZnO as functions of (a) S parameter and (b) L_d . Sample identification is written in the order of growth direction, T_g in bracket and substrate material.

as a function of τ_{PL} at 293 K obtained by TRPL in figure 7: in figure 7, sample identification is written in the order of growth direction, T_g , and substrate material. The values of L_d for both the epilayers and the bulk crystal were much shorter than the typical one (about 200–300 nm) in nearly defect-free materials such as Si [63] and GaAs [64] and close to that in very low threading dislocation density GaN [34]. As shown in figure 7, all the epilayers exhibited larger S and shorter L_d compared with those of the bulk crystal, indicating the presence of a larger number (greater size) of positron trapping centres (neutral and negatively-charged V_{Zn} and V_{Zn} complexes) and positron scattering centres (positively charged V_O , Zn_i , O_i and complexes). For ZnO/SCAM, S tended to decrease with the increase in T_g [30] and the smallest value was obtained from the film grown at 800 °C, although L_d was the shortest: the homoepitaxial layers exhibited smaller S parameters but relatively short L_d [30]. From the results, the increase in T_g and lattice matching were considered to be effective in reducing the S parameter (V_{Zn} density). This observation was consistent with the reduction of nonradiative defect density with increasing T_g for ZnO/SCAM, which was concluded from the results of TRPL measurements, as revealed from figures 6(b) and (c). It should be noted from figure 6(d) that S parameters of (000 1) homoepitaxial films and (1 1 $\bar{2}$ 0) film were comparable to those of (000 $\bar{1}$) homoepitaxial films. The results implied that the growth polar direction had negligible influence on the incorporation of V_{Zn} , the result being different from the case for GaN that incorporation of impurities [65] as well as V_{Ga} and $V_{Ga}-O$ defect complexes was enormously enhanced for the [000 $\bar{1}$] polar growth [34].

To discuss the origin of nonradiative defects existing in unintentionally doped ZnO, τ_{PL} at 293 K, which is the representative of τ_{nr} , is plotted as functions of S and L_d in figures 7(a) and (b), respectively. As shown, the nonradiative lifetime increased with the decrease in S and the increase in L_d . The former means the reduction in V_{Zn} -related negatively charged defect density and the latter means the reduction in

gross density of positively charged, negatively charged and neutral point defects. Because τ_{nr} did not have a perfect correlation with T_g or growth orientations, the dominant parameter that limits τ_{nr} and thereby emission efficiency η at 300 K must be the gross density of point defects, which are incorporated with V_{Zn} and may be localized around structural defects. Certain defects such as V_{Zn} -defect complexes are the most probable candidates. Here, we should mention that TRPL measurements were carried out by monitoring the near-band-edge excitonic PL peak, and therefore τ_{PL} includes both the real τ_{nr} and carrier transfer time to deep defect levels such as V_O , Zn_i , V_{Zn} and V_{Zn} -defect complexes. Apparently, some of them are radiative defects (origin of green luminescence band: GL), but they reduce the experimental τ_{nr} . However, there exist other V_{Zn} -defect nonradiative recombination centres, since τ_{nr} of the samples that do not exhibit the GL band also obeyed the tendency shown in figure 7.

From figures 6(b) and 7, τ_{nr} was found to increase with increasing T_g for ZnO/SCAM samples. In order to tremendously improve η in ZnO epilayers at 300 K, high-temperature growth experiments were carried out using the high-temperature-annealed ZnO self-buffer layers [27] on SCAM substrates, since T_g of the sample sets shown in figures 6 and 7 was much lower than the typical one for GaN growth (typically 1050–1100 °C [39]). Details of the self-buffer preparation procedure have been given in [27]. Because L_d of ZnO/SCAM grown at 800 °C was shorter than those grown around 600 °C (but S was smaller), as shown in figure 7, nonequilibrium incorporation of positron scattering centres such as interstitials and V_O was probable during higher temperature growth. To suppress the enhanced incorporation of those positively charged defects, post-growth annealing was carried out simultaneously. Values of τ_{PL} at 293 K of 500–1000 nm-thick ZnO films are plotted as functions of T_g , cooling rate and ambient O₂ pressure during cooling in figure 8. Note that the excitation power for the TRPL measurements was reduced to 3 mW (80 MHz repetition rate) to realize the weak excitation regime, in which the exciton density would be lower than the overall nonradiative defect density to compare τ_{nr} , since τ_r of electron–hole plasma is much shorter than that of exciton spontaneous emission. As shown, τ_{nr} tended to increase with the increase in T_g and decrease in cooling rate and ambient O₂ pressure. The value reached up to 3.8 ns for $T_g = 1020$ °C and cooled at 10 °C min⁻¹ in 10⁻⁶ Torr O₂ ambient. This value is the longest spontaneous emission lifetime at room temperature ever recorded in ZnO. These results imply that for intermediate T_g up to 1000 °C, those interstitials out-diffused during post-growth cooling under near vacuum. Indeed, L_d of the samples exhibiting long τ_{nr} increased up to 50 nm or longer (the film thickness of approximately 1 μ m was too thin to obtain the ‘flat’ region in the S – E curve), which is comparable to that in the bulk ZnO. For the lowest O₂ pressure of 10⁻⁹ Torr (background O₂ in the chamber), the annealing higher than 1000 °C caused the decrease in τ_{nr} , which may be due to additional introduction of vacancy-type point defects and dissociation of ZnO epilayers. A possibility of improving τ_{nr} and hence η of exciton emissions at room temperature was shown using high T_g and appropriate defect management. Since p-type ZnO was realized using the repeated-temperature

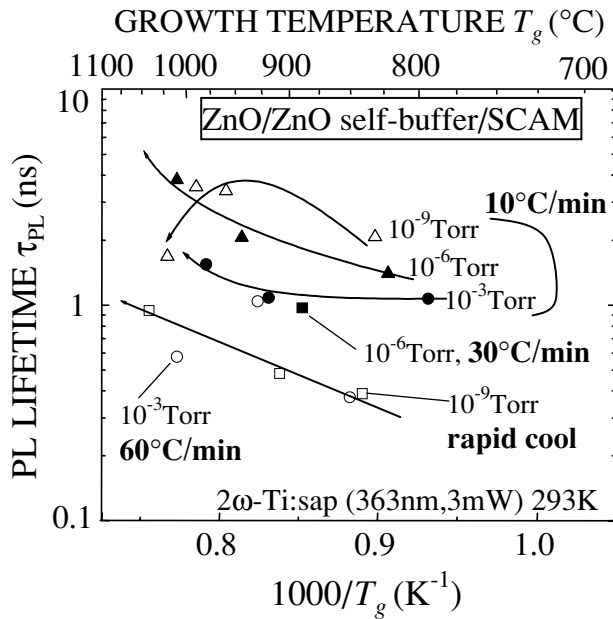


Figure 8. TRPL decay constants of the near-band-edge excitonic PL peak at 293 K, which in general determine the time-integrated intensity at room temperature, in ZnO epilayers grown on high-temperature-annealed ZnO self-buffer layers on SCAM substrates [27]. The epilayers were annealed during cooling after the growth under different cooling rates and ambient O_2 pressures.

modulation epitaxy [26], in which N atoms were doped at low T_g and the crystal quality was recovered during subsequent high T_g growth, this defect management technique will enable us to observe polariton laser effect in the near future.

4. Conclusion

Static and dynamic responses of excitons in state-of-the-art bulk and epitaxial ZnO were reviewed to support the possible realization of polariton lasers. The following four important topics were treated to view current issues and to indicate a way of improving the epilayer quality: (i) exciton-polariton structures in bulk and epitaxial ZnO were resolved at 8 K, and the energies of PR resonances corresponded to those of UPB and LPB, where A-, B- and C-excitons couple simultaneously to an electromagnetic wave. PL peaks due to the corresponding polariton branches were observed, and ω_{LT} of the corresponding excitons were obtained to be 1.5, 11.1 and 13.1 meV, respectively. The latter two values are more than two orders of magnitude greater than that of GaAs, being 0.08 meV. (ii) Using those values and material parameters, the corresponding Ω_{Rabi} of exciton-polaritons coupled to a model MC mode was calculated to be 191 meV, which is the highest value ever reported for semiconductor MCs. The value satisfies the requirements to observe the strong exciton-light coupling regime necessary for polariton lasing above room temperature. (iii) Polarized OR and PR spectra of an out-plane nonpolar (11 $\bar{2}$ 0) ZnO epilayer were measured, because ZnO QWs grown in nonpolar orientations are expected to show higher emission efficiencies due to the elimination of spontaneous and piezoelectric polarization fields normal to the QW plane. They exhibited in-plane anisotropic exciton

resonances according to the polarization selection rules for anisotropically-strained wurzite material. (iv) Impacts of point defects on the nonradiative processes in L-MBE ZnO were studied: free excitonic PL intensity at room temperature naturally increased with the increase in τ_{nr} . The value of τ_{nr} increased and density or size of V_{Zn} defects decreased with the increase in T_g in heteroepitaxial films grown on SCAM substrate, and the use of homoepitaxial substrates further reduced V_{Zn} density. The value of τ_{nr} was shown to increase with the decrease in gross density of positively and negatively charged and neutral point defects including complexes rather than with the decrease in V_{Zn} density. The results indicate that the nonradiative recombination process is governed not by single point defects, but by certain defects introduced with the incorporation of V_{Zn} , such as V_{Zn} -defect complexes. As a result of defect elimination by growing the films at high T_g followed by subsequent post-growth *in situ* annealing, combined with the use of a high-temperature-annealed ZnO self-buffer layer, a record long τ_{nr} for the spontaneous emission of 3.8 ns was obtained at room temperature. By using progressively improving epitaxial growth methods, the polariton laser effect due to Bose condensation will be observed at room temperature in the near future.

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