Optical properties of excitons in ZnO-based quantum well heterostructures

T Makino$^{1,4}$, Y Segawa$^{1,4}$, M Kawasaki$^{2,5}$ and H Koinuma$^{3,5}$

$^{1}$ Photodynamics Research Center, RIKEN (The Institute of Physical and Chemical Research), Aramaki-aza-Aoba 519-1399, Sendai 980-0845, Japan
$^{2}$ Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
$^{3}$ Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan
$^{4}$ Department of Physics, Tohoku University, Sendai 980-8577, Japan
$^{5}$ Also a member of Combinatorial Material Exploration, Japan Science and Technology Corporation, Tsukuba, Japan.

E-mail: tmakino@postman.riken.go.jp

Received 15 September 2004
Published 15 March 2005
Online at stacks.iop.org/SST/20/S78

Abstract

Recently the developments in the field of II–VI-oxides have been spectacular. Various epitaxial methods have been used to grow epitaxial ZnO layers. Not only epilayers but also sufficiently good-quality multiple quantum wells (MQWs) have been grown by laser molecular-beam epitaxy (laser-MBE). We mainly discuss the experimental aspect of the optical properties of excitons in ZnO-based MQW heterostructures. Systematic temperature-dependent studies of optical absorption and photoluminescence in these MQWs were used to evaluate the well-width dependence and the composition dependence of the major excitonic properties. Based on these data, the localization of excitons, the influence of exciton–phonon interaction and quantum-confined Stark effects are discussed. The optical spectra of dense excitonic systems are shown to be determined mainly by the interaction process between excitons and biexcitons. The high-density excitonic effects play a role in the observation of room-temperature stimulated emission in the ZnO MQWs. The binding energies of exciton and biexciton are enhanced from the bulk values, as a result of quantum-confinement effects.

1. Introduction

ZnO has a large fundamental band gap of $\sim3.37$ eV at room temperature [1–3]. The nature of high thermal conductivity, high luminous efficiency and mechanical and chemical robustness has made ZnO and its alloys the promising material system for light-emitting devices operated at a UV spectral region [4]. New applications for ZnO field effect transistors are also under extensive exploration [5–9]. In addition to these stabilities, ZnO has the advantage of a larger exciton binding energy [10] (about 60 meV), which assures more efficient excitonic emission at higher temperatures. Moreover, the excitons in ZnO-based quantum well (QW) heterostructures exhibit strong stability as compared to bulk semiconductors or III–V QWs due to the enhancement of the binding energy [11, 12] and the reduction of the exciton–phonon coupling [13] caused by quantum confinement. Due to these effects, excitons are expected to play an important role in many-body processes such as laser action and nonlinear absorption of II–VI-oxide QWs even at room temperature. For example, excitonic gain has been demonstrated in ZnO/ZnMgO QWs. A detailed study of excitons in ZnO multiple quantum wells (MQWs) is thus important for understanding the optical properties of these wide gap heterostructures, especially in view of their application to ultraviolet–blue optoelectronic devices [14]. In addition, the effect of built-in electric fields inside QW layers might be taken into account for ZnO QWs having a relatively high barrier height. As has been extensively investigated in
wurtzite GaN-related heterostructures, in biaxially strained wurtzite heterolayers with the c-axis parallel to the growth direction, piezoelectric and spontaneous polarization effects may be present as a consequence of its noncentrosymmetry [15–19].

In this paper, we overview the most recent experimental and theoretical work about the optical properties of excitons in ZnO-based QWs grown on lattice-matched ScAlMgO4 (SCAM) substrates. In section 2 we briefly introduce various wide-gap materials that have been used to construct the ZnO-related double heterostructures. In section 3 we briefly summarize the basic theoretical concepts used to model quasi-two-dimensional excitons in QWs. In sections 4 and 5 we discuss the linear properties of optical excitons, including the thermal stability, the strength of the quantum-size and the quantum-confined Stark effects in QWs, and the temporal evolution of the excitonic transitions. In section 6 we examine the nonlinear optical properties of excitons. After a short theoretical introduction, in subsection 6.2 we discuss the role of excitons in the stimulated emission processes of II–VI-oxide QWs. Finally, we also discuss the enhancement in biexciton binding energy and the stimulated emission from two-component carrier plasmas (i.e., electron–hole plasmas). Our conclusions are drawn in section 7.

2. Various zinc oxide-related double heterostructures

Various wide-gap semiconducting or insulating materials have been adopted to construct ZnO-related heterostructures. Since this paper is devoted to the optical properties of the QWs, we concentrate on the materials adopted for the double heterostructures. Amongst them, the ZnO/ZnMgO double heterostructure is a quantum structure that has been most extensively studied with spectroscopic characterization. Resonant tunnelling action was observed in a similar QW [20]. Because the stable crystal symmetry of ZnO is different from that of MgO or CdO, the growth of these ternary alloys over the whole concentration range is rather difficult. We should here emphasize the almost perfect lattice mismatch attained between CdZnO and MgZnO. This ternary–ternary QW can realize a perfect (in-plane) lattice match with a maximum barrier height up to 0.9 eV by choosing an appropriate combination of cadmium and magnesium concentrations (cf figure 4 in [21]) [21, 22]. This is an advantage compared to (In,Ga)N/(Al,Ga)N QWs. Not only wurtzite nitrides [23, 24] such as GaN or AlN but also oxides-based insulators are found to be good candidates for the barriers of the QWs. Ohkubo et al [25] reported the growth and the optical characterization of β-LiGaO2/ZnO/ScAlMgO4. Fujimura et al [26] reported the growth of the heterostructures based on diluted magnetic semiconductors, ZnO/ZnMnO. Bogatu et al claimed the existence of surface QW-like states in hydrogen-implanted ZnO crystals [27].

3. Modelling of excitonic states in ZnO quantum wells

In this paper, we concentrate on II–VI oxide QWs consisting of binary compounds ZnO, MgO, CdO and their solid solutions ZnMgO and ZnCdO because many spectroscopic studies have been conducted in these systems [28]. The combination of these isoelectronic materials (ZnO, MgO, CdO) spans the whole blue–ultraviolet spectral range (figure 1), though with the complication of lattice mismatch which strongly affects the electronic states and the valence band offset. The calculation of the confinement energies and excitonic states requires a detailed knowledge of the band structure parameters. We should mention that most of the band parameters of ZnO and MgO and related ternary alloys are not well known. Those used in this paper [10] are summarized in table 1. It should be pointed out that the MgZn1−xO alloys grown with wurtzite symmetry and the physical parameters available in the literature are for MgO which grows with zincblende symmetry thus making it impossible to determine the values of physical parameters in the alloy system by interpolation. Because the effective masses or dielectric constants are not known for MgO, those for the solid solutions are also not known. On the other hand, the band gap energy in MgZn1−xO has been given elsewhere [29]. Coli and Bajaj [30] deduced a reliable band gap offset since so far there have been no reliable experimental determinations of the ratio between the conduction and valence band offsets (ΔEc/ΔEv) in these heterostructures [14, 31]. They have used ΔEc/ΔEv as a fitting parameter, varying it from 90/10 to 60/40 and found that their results are closer to the experimental data when the ratio is in the range of 60/40–70/30. The electronic states are evaluated in the effective mass approximation.

The exciton binding energy is a very important parameter to be evaluated in II–VI-oxide compounds. The enhancement of the excitonic stability due to quantum confinement [11, 12] and reduced phonon coupling [13] is one of the most interesting properties of II–VI-oxide QWs for optoelectronics. It is necessary from technological viewpoints to correctly
describe the well width and composition dependencies of the excitonic binding energy.

Coli and Bajaj also calculated the excitonic transition energies in ZnO/MgZnO QW heterostructures, accounting for the effects of the exciton–phonon interaction in the calculation of the exciton binding energies as formulated by Pollmann and Büttner [32]. Figure 2 shows their results, describing exciton binding energy as a function of well width and of Mg concentration. Type-I QWs such as ZnO/MgZnO exhibit binding energies ranging from the bulk value (about 60 meV) up to ≈120 meV or more, depending on the well depth (barrier height) and well width (figure 2). In section 5 we will compare the calculated exciton binding energies with the available experimental data.

Another important merit of the ZnO-based MQWs is the considerable enhancement of the optical absorption strength. For light propagating perpendicular to the basal plane of the QW, the integrated absorption strength is significantly larger than the corresponding values of II–VI (ZnSe) or III–V (GaAs) QWs. This finding together with the extremely large exciton binding energy suggests that excitons play a very important role in the linear and nonlinear optical responses of ZnO-based QWs. It is therefore very important to have a precise description of the excitonic properties in order to understand some of the relevant optoelectronic phenomena of interest for modern technology, e.g., lasing, optical modulation and nonlinear switching.

4. Polarization in wurtzite II–VI-oxides

A wurtzite structure does not have any symmetry operation that laps the c-axis bond parallel to the [0001] directions on the bond of other oblique directions one over the other. Consequently, wurtzites can possess spontaneous polarization without breaking their symmetry. In ZnO like GaN, a double layer coupled in an oblique direction displaces so that laps the interface cancels this sheet charge, these polarization fields give rise to a potential difference on the opposite sides of the well, the magnitude of which is proportional to the well layer thickness (L_w).

As is well known, spontaneous polarization and piezoelectric polarization have played a crucial role in the optical properties of nitride-based heterostructures and devices. On the other hand, despite the same crystal structure, it has been believed that these effects are not very serious in the case of ZnO-based QWs, because the lattice mismatch between the barrier and well layers is much smaller than that of nitride-based heterostructures. Such an argument is correct as long as the contribution from the piezoelectric polarization is discussed.

Figure 3 compares the piezoelectric polarization fields as a function of magnesium or indium concentration. The data for In_Ga_N/GaN are from [32–33]. On the other hand, we must bear in mind the possibility of spontaneous polarization mismatches at the interfaces if the fact that the spontaneous polarization of ZnO is comparable with that of GaN or AlN is considered. Unfortunately, there are no reports on the spontaneous polarization coefficient of MgO or MgZnO alloys. Optical transition energy, oscillator strength and recombination times crucially depend on the magnitude of polarization fields due to the quantum-confined Stark effects.

5. Linear optical properties of quasi-two-dimensional excitons

5.1. Optical absorption

Representative low-temperature absorption spectra of selected ten-period ZnO/MgZnO MQWs are shown in figure 4. The samples investigated here were grown by laser molecular-beam epitaxy on ScAlMgO substrates. The detailed growth procedure has been given elsewhere [31]. The PL and absorption spectra in a 500 Å thick ZnO epilayer on SCAM
were included for comparison [36]. The width of these ZnO samples spans the range from bulk-like behaviour (47 Å) to the quasi-two-dimensional limit (7 Å). The exciton Bohr radius of ZnO is \( \approx 18 \text{ Å} \) [10]. The combination of these compositional and configurational parameters permits a fine-tuning of the excitonic properties of the ZnO MQWs, which can be investigated by systematic optical and structural studies. The absorption energy of the localized excitonic feature from the barrier layers is shown by a horizontal arrow. Spectra in a 500 Å thick ZnO film are also shown. A, B indicates A- and B-exciton absorption bands, I\(_0\) shows the PL of a bound exciton state, B+LO, B+2LO, and B+3LO correspond to exciton–phonon complex transitions, \( n = 1 \) shows the lowest excitonic absorption of the well layers, and \( n \geq 2 \) means the excited states of the exciton or higher interband (sub-band) transitions.

Figures 5(b) and (c) show the well width dependence of the peak energies of PL (closed circles) and absorption (open squares), respectively, in ZnO/M\(_{27}\text{ZnO}_{73}\)O and ZnO/M\(_{27}\)ZnO MQWs on SCAM substrates. Energy diagrams of conduction and valence bands between barrier and well layers in ZnO/M\(_{27}\)ZnO MQW [31]. The upward arrow shows the lowest interband transition. Peak energies of PL (circles) and absorption (squares) are plotted against \( L_w \) for ZnO/M\(_{27}\)ZnO MQW. A solid curve is shown as a visual guide.

Figure 4. Absorption (continuous lines) and photoluminescence (shaded) spectra of different ZnO/M\(_{12}\)ZnO MQWs at 5 K. The well widths (\( L_w \)) are: (a) 47 Å, (b) 17.5 Å and (c) 6.91 Å. The absorption energy of the barrier layers is shown by a horizontal arrow. Spectra in a 500 Å thick ZnO film are also shown. A, B indicates A- and B-exciton absorption bands, I\(_0\) shows the PL of a bound exciton state, B+LO, B+2LO, and B+3LO correspond to exciton–phonon complex transitions, \( n = 1 \) shows the lowest excitonic absorption of the well layers, and \( n \geq 2 \) means the excited states of the exciton or higher interband (sub-band) transitions.

Energy diagrams of conduction and valence bands between barrier and well layers in ZnO/M\(_{12}\)ZnO MQW [31]. The upward arrow shows the lowest interband transition. Peak energies of PL (circles) and absorption (squares) are plotted against \( L_w \) for ZnO/M\(_{27}\)ZnO MQW (b) and ZnO/M\(_{12}\)ZnO (c) QWs. A solid curve is shown as a visual guide.
of these x-ray patterns provides the information on well width and composition. High crystallinity and high-thickness homogeneity are evidenced by Bragg diffraction peaks (closed triangles) and clear intensity oscillations due to the Laue patterns.

A line shape analysis of the satellite peaks reveals some inhomogeneous fluctuation presumably caused by a smooth long-range modulation of the QW thickness. Such an effect produces relevant potential modulation in the QW causing carrier or exciton localization. As stated above, this localization dramatically affects the optical properties of ZnO QWs. For ZnO/ZnMgO QWs, it is unnecessary to consider the effects [37] of interface diffusion of Mg whereas the formation of ternary alloys at the interface of binary QWs has been experimentally investigated in ZnSe-related QWs [38].

The interactions of electrons with phonons have been demonstrated to greatly affect the optical and electrical properties of semiconductors [39–41]. The temperature dependence of the absorption spectra also provides information on the thermal stability of excitons [13]. In figure 7, we show absorption spectra in the 5–300 K temperature range for MQWs with $x = 0.12$ and $L_w = 47$ Å. As can be seen from the figure, even a shallow QW (lower Mg content) exhibits room-temperature excitonic absorption. The thermal stability of the excitons depends on the ratio of the exciton binding energy to the longitudinal optical phonon energy, and on the actual strength of the exciton–phonon coupling [41]. The latter parameter can be approximately estimated from the temperature-dependent absorption linewidth of the ground-level exciton states.

An increase in linewidth of the exciton is observed in the temperature-dependent absorption spectra. Figure 8(a) shows the temperature dependence of the FWHM of the excitonic absorption peak for a sample with $L_w = 47$ Å. Thermal broadening of the excitonic absorption peak is generally interpreted as being due to an exciton–phonon interaction. The exciton–phonon interactions ionize the exciton into a free electron and hole in the continuum of states or scatter the exciton into (higher-lying) discrete exciton states [13]. According to Segall’s expression [40], the total linewidth of the exciton contains two contributions: inhomogeneous broadening and homogeneous broadening. Within the adiabatic approximation the temperature dependence of the full width at half maximum (FWHM) can be approximately described by the following equation:

$$\Gamma(T) = \Gamma_{\text{inh}} + \gamma_{pb} T + \Gamma_{\text{LO}} \left[ \exp\left(\frac{h\omega_{\text{LO}}}{k_B T}\right) - 1 \right],$$

(1)

where $\Gamma_{\text{inh}}$ is the temperature-independent term that denotes the inhomogeneous linewidth due to the exciton-exciton, exciton-carrier interaction [40], and the scattering by defects, impurities and the size fluctuations. The second term $\gamma_{pb} T$
Figure 9. The width of 5 K excitonic PL lines versus $L_w$ in ZnO-based QWs for $x = 0.12$ and $x = 0.27$. The open circles are estimated from the QCS PL bands.

is due to the acoustic phonon scattering. The $\gamma_{ph}$ represents the acoustic phonon coupling strength, mainly caused by the deformation potential mechanism. At low temperatures, since the population of the longitudinal-optical (LO) phonon is vanishingly small, the scattering is mainly ruled by acoustic phonons. The third term is the linewidth due to the LO phonon scattering. $\Gamma_{LO}$ is the exciton-LO phonon coupling strength, and $\hbar\omega_{LO}$ is the LO-phonon energy. At high temperatures, the LO phonon Fröhlich scattering dominates.

The solid line represents the fitted result based on equation (1). The best fit is obtained for the parameter values $\Gamma_{inh} = 17$ meV, $\gamma_{ph} = 31$ meV/K, and $\Gamma_{LO} = 341.5$ meV. Here, we take $\hbar\omega_{LO}$ to be 72 meV, equal to that of bulk ZnO. The value of $\hbar\omega_{LO}$ does not exhibit an obvious change of well width for the MQWs as determined by the PL spectra.

We summarize $\Gamma_{LO}$ for different QW widths in figure 8(b). As a comparison, $\Gamma_{LO}$ for a ZnO epitaxial layer was included. The exciton–phonon coupling in all the QWs ($L_w \leq 47 \text{Å}$) assessed here is found to be smaller than in bulk ZnO. In addition, they monotonically decrease with decreasing $L_w$.

We assigned this variation to the enhancement of the exciton binding energy. As stated above, $\Gamma_{LO}$ is also dependent on the ratio of the exciton binding energy to the longitudinal optical phonon energy. For bulk ZnO, the exciton binding energy is much smaller than that of LO phonon. On the other hand, this is no longer the case for ZnO multiple quantum wells (MQWs): the binding energy exceeds the $\hbar\omega_{LO}$. A similar effect was also observed in other QW systems [41]. The important implication of this result is that the reduced exciton–phonon coupling in QWs favours the exciton stability leading to a dominant excitonic role in the optical processes of ZnO QWs under strong injection or high temperatures.

Figure 10. Line-shape fitting of the absorption spectrum at 5 K of a ZnO/ZnMgO MQW with $L_w = 9$ Å. The simulation result (dashed line) and the experimental data (solid line) are shown. Note that the A- and B-exciton structures here were not spectrally resolved.

In order to get information on this important parameter and more in general on the excitonic eigenstates and binding energy one has to model the absorption line shape with the modified Elliot two-dimensional (2D) exciton model [46, 47]. It is well known that the reduction of the dimension modifies the excitonic line shape which is characterized by the enhancement of excitonic binding energies and by the concentration of the density-of-states into the discrete excitonic peak. For purely two-dimensional excitons this was first calculated by Shinada and Sugano [48]; such a purely 2D formulation has been used in this work for simplicity. Analytical expression including the broadening effect has been deduced in [46, 47] and is used here for the simulation. For example, the step-like continuum of the QW density of states is simulated by a step function, convoluted with a Lorentzian broadening used to reproduce the exciton factor at the band edge. An example of the result of this line-shape simulation is shown in figure 10 for a ZnO/ZnO/Mg$_{0.27}$Zn$_{0.73}$O MQW with $L_w = 9$ Å. The parameters used in the simulation are the band gap energy of $E_g$, the excitonic binding energy of $E_b^{ex}$, and the damping parameter of $\Gamma$. The value of $E_g$ was 3.54 eV deduced from the lowest excitonic line, whereas the $E_b^{ex}$ of 72 meV was cited from the results of theoretical work [30]. The damping parameter of 24–25 meV was deduced from the width of the excitonic absorption peak. The calculated absorption spectrum (dashed line) reproduces well the experimental spectrum (solid line) for the line shape of the lowest excitonic absorption, whereas above the excitonic line, the calculation is not in good agreement with the experimental data. There are two plausible reasons for this poor agreement. First, the tailing contribution of the localized excitonic states of the barrier (MgZnO layers) should be pointed out. It is, however, difficult to quantitatively estimate the contribution of the barrier absorption. Second, the approximation of pure two-dimensional excitons is also responsible for that: one has to know quantitatively the realistic degree of anisotropy of our QW (i.e., the Sommerfeld factor).

Because of the above-mentioned disagreement, the experimental exciton binding energy is extracted from the energy positions of the stimulated emission as a result of exciton–exciton scattering and is summarized in figure 11 for ten different MQWs (open circles and closed squares for
Experimental exciton binding energy of ZnO/ZnMgO QWs with $x = 0.12$ (circles) and $x = 0.27$ (triangles) as a function of the well width. The curves (solid and dashed lines) are the results of the variation calculations [30].

$x = 0.12$ and $x = 0.27$ QWs, respectively, together with the results of the variational calculations (solid and dashed lines) described in section 3. The method of evaluation will be described later in section 6. For shallower MQWs, the calculated exciton binding energy varies approximately from the bulk value (about 70 meV for $L_w = 47\,\text{Å}$) up to 86 meV for $L_w = 18\,\text{Å}$. For even lower well width, the calculated exciton binding energies decrease due to the increased penetration of the exciton wavefunction in the barriers. Deeper QWs ($x = 0.27$) exhibit a similar behaviour, but the maximum exciton binding energy reported is 115 meV. The experimental results are in good agreement with the theoretical calculation. The calculated exciton binding energy matches within 5 meV the experimental values in the case of the $x = 0.12$ MQW (open circles and continuous line). The reasonable overall agreement between the calculated and measured binding energies supports the choice of polaron masses and dielectric constants used here.

These results clearly show that exciton confinement in ZnO/ZnMgO MQWs can be tuned independently by varying the well composition ($x$) or thickness ($L_w$). Based on the experimental data, for a given well width of 37 Å, the increase of the well width (the increase of the Mg content from typically $x = 0.12$ to $x = 0.27$) results in a 14% enhancement of the exciton binding energy, reflecting the enhanced localization of the carrier wavefunctions in the well.

In figure 12, we compare the calculated exciton resonance energies with the experimental values (closed circles and open squares). We should emphasis again the importance of exciton–phonon interaction in these polar semiconductor QWs, because there is better agreement between the results of their calculations (lines) and the experimental data if the calculation takes that effect into account.

Before concluding this subsection we discuss the line shape of photoluminescence excitation (PLE) spectra taken for an MQW grown on a sapphire substrate. There has been few experimental reports of the PLE spectroscopy because the lattice matched ScAlMgO substrate is transparent for the wavelength region of interest. In a QW of the weak confinement regime such as the ZnSe/ZnS QW, strong hot exciton features are observed in the PLE spectra. Such an oscillatory behaviour with a period equal to the LO phonon energy has often been observed in bulk semiconductors. The oscillatory structure was not observed in the PLE spectrum taken for a ZnO MQW [31], indicating a significant reduction of the exciton–phonon coupling (the Huang–Rhys factor) with respect to bulk ZnO.

5.2. Temporal evolution of the excitonic transitions

In this subsection we discuss the transient properties of excitons confined in ZnO-based QWs. Only time-resolved PL experiments have been performed for ZnO/Zn$_{0.88}$Mg$_{0.12}$O and ZnO/Mg$_{0.7}$Zn$_{0.3}$O MQWs in which it is unnecessary to take the internal electric field effects into account. In optical experiments, excitons are formed with some excess energy by the off-resonant pumping. The excess energy is relaxed in a few hundreds fs by the exciton–LO phonon interaction, resulting in a quasi-equilibrium distribution of thermalized excitons. After this the short transient excitons undergo a number of different interactions, namely localization at potential fluctuations, scattering with electrons or other excitons and eventually they recombine radiatively on a time scale of the order of a few hundreds ps.

On the time scale of the exciton lifetime the behaviour of the ZnO QWs does not differ appreciably from that of other II–VI or III–V structures. In figure 13, we display the spectral distribution of decay time in ZnO/ZnMgO MQW structures of well width 7, 13, 18, 42 Å and Mg content $x = 0.12$.

The time-resolved PL experiments provide important information on the localization of excitons within the inhomogeneously broadened density of states caused by monolayer fluctuation and disorder in the ternary alloy barriers. As a general trend the temporal evolution of the...
luminescence from localized excitons exhibits decay times longer than for the free excitons. This is clearly seen in the low energy tail of the exciton resonance of ZnO/ZnMgO MQWs. The estimated PL decay time is a monotonically decreasing function of the emission energy. This is because the decay of the localized excitons is not only due to radiative recombination but also due to the transfer process to the tail state. An analysis of the time-resolved luminescence traces provides the density of localization centres existing in the QW.

Results of best fits have been given in [50]. It is found that the decay times \( \tau(E) \) dependences of the localization depth \( L_w \) with respect to each other (cf figure 3 of [50]). Therefore, the \( L_w \) dependence of \( \tau(E) \) can be expressed by the following equation [49]:

\[
\tau(E) = \frac{\tau_{pl}}{\exp((E - E_{me})/E_0)},
\]

where \( E_0 \) shows the degree of the depth in the tail state and \( E_{me} \) is the characteristic energy representing the absorption edge. Results of best fits have been given in [50].

Optical properties of excitons in ZnO-based quantum well heterostructures

5.3. Quantum-confined Stark effects observed in ZnO quantum wells

It is not necessary to take the quantum-confinement Stark (QCS) effect into account in the case of the ZnO/Mg\(_{0.12}\)Zn\(_{0.88}\)O MQWs. In the case of \( x = 0.27 \) in which the lattice mismatch between the well and the Mg\(_{0.12}\)Zn\(_{0.88}\)O barrier layers is relatively large, since the directions of spontaneous and piezoelectric polarizations along the ZnO wells are coincident with respect to each other, the electric-field induced inclination of the band profiles is considered to become significant. Figure 14 shows 5K PL spectra corresponding to ZnO/Mg\(_{0.12}\)Zn\(_{0.88}\)O QW samples with three different \( L_w \). Only the LE band was observed in ZnO/Mg\(_{0.12}\)Zn\(_{0.88}\)O QWs with \( L_w \) smaller than 38 Å. Increasing \( L_w \) yielded a different observation: other than zero-phonon peaks of the LE bands, now there is another prominent PL peak (denoted by QCS) in the 47 and 42 Å thick QWs, which seem to have different origins with the LE band. These QCS bands have larger Stokes shift than that of LE bands. These PL bands are located \( \approx 40 \) meV in energy below the emission band of the localized excitons and
≈60 meV below the absorption energy of the free exciton transition. Calculations of the absorption energies [30] are shown by arrows in figure 14.

We think that the magnitude of the electric field in the case of $x = 0.27$ is larger than that of $x = 0.12$, because of the larger lattice mismatch between ZnO and Mg$_{0.27}$Zn$_{0.73}$O (cf figure 3 in section 4). This internal field, present along the growth axis of the system, is caused by piezoelectric and spontaneous polarizations. It is considered to be easier to observe the QCS bands in the sample with higher Mg concentration. Therefore, this band is attributed to be due to the radiative recombination from the excitons influenced by the internal electric field. The Stokes-like shift of PL is due to the quantum-confined Stark effect induced by the internal electric field. If there is a sizable polarization field inside a QW with small lattice mismatch between the barrier and well layers, the spontaneous polarization mismatch at interfaces is more likely to be responsible. We cannot, however, discuss this contribution because the spontaneous polarization coefficient of MgO has not been reported so far.

Why did the QWs with $L_w$ of 7–38 Å not show the QCS emission? A band diagram of QWs under both the piezoelectric and spontaneous polarization fields is schematically shown in figure 14(d). The PL energy of the QCS bands is lower than that of the LE. Nevertheless, in the case of small $L_w$, the energy difference can be neglected because the depth of the triangle-shaped potential well is smaller than the case of larger $L_w$. Both the electron and hole wavefunctions are confined in the wells even when the electric field is present. Thus, the overall Stokes-like shift of the PL is thus determined only by the in-plane (lateral) band gap inhomogeneity. We observe the single PL peak (LE band) in this case. On the other hand, in the opposite case (larger $L_w$), the depth of the triangle-shaped potential well becomes larger. Carrier wavefunctions drop into these triangle-potentials on one side of the well layer. The electric field pushes the electron and the hole towards opposite sides of the well. Thus, the energy difference between QCS and LE becomes sizable ($\approx 40$ meV).

It is now known that the quantum-confined Stark effects somewhat reduce the excitonic oscillator strength. The distinct excitonic peak could not be observed in a 5K absorption spectrum taken for a 42 Å thick QW. However, this was possible for an 18 Å thick QW. Such a disappearance may be explained by the quenching oscillator strength. It has been demonstrated, similarly to GaN, that the magnitude of piezoelectricity is larger than zincblende semiconductors and that there are effects of spontaneous polarization that are absent in zincblende semiconductors. More detailed theoretical work is desired to determine the magnitude of the electric field.

5.4. LO phonon replica in ZnO/Mg$_{0.27}$Zn$_{0.73}$O QWs

An important result of the exciton–phonon interactions in semiconductors is the appearance of phonon-assisted emissions of excitons in the luminescence spectra. In the past decades, phonon replicas have been observed in the PL spectra in most II–VI semiconductors [51–53] and in some ionic crystals [40]. The intensities of these replicas relative to the zero-phonon peak depend strongly not only on the exciton–phonon coupling strength but also on the internal electric field in the QW layers. We have already discussed the latter effect in section 5.3. The distribution of emission intensities between phonon replicas and the main emission peak reflects the coupling strength with the LO phonons and is described in terms of the Huang–Rhys factor.

We give another piece of supporting evidence of our spectral assignment for QCS bands by paying attention to the intensity distribution of LO phonon replicas. The 1LO and 2LO phonon replicas of the QCS bands (e.g., QCS–LO) are clearly seen in figures 14(a) and (b). This is not the case for the localized exciton emission as shown in figure 14(c). The $L_w$ dependence of the PL intensity ratio has been given elsewhere [54, 55]. The coupling strength of the electron–hole pairs separated due to the quantum-confined Stark effect (QCS) with the LO phonons is significantly larger than that of the localized excitons.

In general, the phonon coupling strength depends strongly on the spatial distributions of electron and hole charge densities and sometimes deviates from the bulk value [56]. The deviation is more outstanding in the cases where the wurtzitic heterostructures are influenced by the strong internal electric field. As shown in figure 14(d), the electrons and holes are distributed on opposite sides along the c-axis direction. The distance between them is not only determined by the Coulomb force but also by the electric field. The reduced overlap of these electron and hole charge densities must be responsible for the observed increase of the coupling strength. It is known that, according to Hopfield [57], the coupling strength is a growing function of the distance between electrons and holes. Conversely, this enhancement supports our spectral assignment concerning the QCS band.

6. Nonlinear excitonic properties

In this section we discuss the nonlinear optical properties of excitons in ZnO-based QWs. Due to the enhanced excitonic stability, nonlinear optical processes involving excitons are very important in those QWs and must be considered relevant even for the design of optoelectronic devices operating with high carrier density and at room temperature. We deal with high-density exciton effects, in which bound electron–hole pair states participate, i.e., the regime of moderately high-excitation intensity is described.

6.1. Basic theoretical concepts

In this subsection, we give a treatment of the two representative recombination processes in dense exciton systems, which play a crucial role for the excitonic nonlinearities of the ZnO epitaxial layers and ZnO-based QWs. We discuss uniquely the following two optical processes caused by the interaction between excitons: (1) exciton–exciton $(x\times x)$ recombination due to their inelastic scattering and (2) biexciton recombination. In these processes only parts of the energy of the recombining exciton leave the QW as a photon, while the remaining energy is transferred to other excitations, such as free carriers or excitons. These processes were first introduced in 1968 for a CdS crystal [58].
6.1.1. Inelastic scattering process of excitons. In the x–x recombination, an exciton is scattered converting into a photon, whereas another exciton is scattered into a state with higher energy (e.g., excited-state excitons or continuum states). Therefore, both energy and momentum are conserved in the total collisional process. The x–x process is a dominant mechanism leading to stimulated emission in ZnO QWs and has been observed at temperatures from 5K up to well above room temperature. The emission line of this assignment has been called P$_n$ ($n$ denotes the quantum number of exciton).

6.1.2. Biexcitons. Since excitons in semiconductors can be understood in analogy to the hydrogen atom, one can expect that excitonic molecules or biexcitons may exist in the same way as H$_2$ molecules. Variational calculations for the biexciton binding energy have been performed as a function of the mass ratio. They give a lower limit of ratio in exciton and biexciton binding energies and indicate that the biexciton is bound in all semiconductors. In the biexciton recombination process, a biexcitonic molecule decays into a photon and a transverse exciton or exciton-like polariton on the lower branch, respectively. The well-width dependence of biexciton binding energy has been estimated experimentally by the low-temperature pump-and-probe spectroscopy. At elevated levels of excitation, stimulated emission related to the presence of a dense neutral electron–hole plasma has been observed. Such a very high-excitation regime will be discussed later.

6.2. Results for the emission due to the inelastic scattering process: role of excitons in the stimulated emission

In this section we start with the experimental results that are related to the x–x recombination process in order to discuss the interplay between excitons recombination in the stimulated emission mechanism of ZnO MQWs. A method to determine the exciton binding energy from this x–x emission will be explained. Because the excitons of ZnO are stable even at room temperature, the x–x inelastic scattering is expected to be seen in the wide temperature range in their MQWs. This process has been observed at intermediate excitation levels in all II–VI compounds investigated so far. The exciton–exciton process can be distinguished spectroscopically by the characteristic energy of their luminescence or stimulated emission. In general, energy and momentum conservation and Boltzman distribution for the excitons are assumed in the scattering process. For example, the typical emission band is displaced from the position of the free exciton to lower energies by approximately one exciton binding energy ($E_b$). Since we would like to discuss its temperature dependence, the resulting emission energy for the exciton–exciton scattering should be written as a function of temperature for the 2D case:

$$\hbar \omega_{x-x} \simeq E_{HH} - E_b - 2\delta k_BT,$$

(3)

with $0 < \delta \leq 1$ where $E_{HH}$ is the free exciton (heavy hole) energy, and $\mu$ is the reduced exciton mass. Typical room temperature spectra in MQWs with $x = 0.12$ and $L_w = 18$ Å are shown in figure 15. This observation corresponds to the demonstration of room-temperature excitonic gain. The P$_n$ lines are observed for the MQWs. Strong and sharp emission peaks were observed at 3.24 eV above a very low threshold ($I_{th} = 17$ kW cm$^{-2}$), and their integrated intensities rapidly increased as the excitation intensity ($I_{ex}$) increased, as can be seen in the inset. Unlike in the case of epitaxial ZnO thin films, a fine structure associated with the P-bands ($P_2, P_4, \ldots$) could not be observed in MQWs probably because of the larger inhomogeneity.

For an unambiguous identification, it is necessary to perform a systematic investigation. In order to facilitate the comparison of the experimental data with equation (3) including the kinetic energy term, we plot in figures 16(b) and (c) the temperature dependence of the peak energy of the P-band in the QWs (Mg concentration of 0.12, $L_w$ of 37 Å and 18 Å). For comparison, a corresponding plot for a thin ZnO film is shown in figure 16(a). At sufficiently low temperatures, the energy separation of the P-band from the resonance energy of exciton must be equal to the exciton binding energy because the kinetic energy approaches zero. The temperature dependence of the peak energy difference in QWs shows the same behaviour as that of ZnO. Thus, as a result of such a careful comparison, it can be said that the mechanism of this stimulated emission for the MQWs is the inelastic x–x scattering. This also rules out other possibilities such as stimulated exciton–phonon scattering as mechanisms leading to this excitonic gain. This method was also used for the determination of exciton binding energies. These estimated values have already been summarized in a previous section (cf figure 11 of section 5), indicating the confinement-induced enhancement.

The x–x recombination process is not only observed in the luminescence, but also in the optical gain spectra. Sun et al experimentally determined the value of the optical gain by using the so-called variable stripe-length method. The peak value of the excitonic gain of a ZnO/Zn$_{0.88}$Mg$_{0.12}$O MQW with $L_w = 18$ Å at room temperature was estimated to be $\approx 250$ cm$^{-1}$.

According to the results of the high-temperature tolerance tests, stimulated emission could be observed up to 377 K, and the characteristic temperature, which is a figure of merit...
with respect to temperature rise, was estimated to be 87 K [59]. This was significantly higher than that of a 55 nm thick ZnO/sapphire (67 K) [60]. The lowest threshold value at room temperature was 11 kW cm$^{-2}$ in the case of $L_w$ of 47 Å. See [59] for details.

6.3. Optical properties of biexcitons

6.3.1. Radiative recombination from biexcitonic states. As has been introduced in a previous subsection, in principle the threshold for laser action using biexcitons as its mechanism is expected to be even lower than that using an x–x scattering process. The reduced binding energy of biexcitons with respect to the exciton, however, makes the biexciton particle rather unstable, so that the room-temperature achievement of biexciton lasing seems to be very difficult even in ZnO MQWs. Nevertheless, the formation of biexcitons has already been found at $T \leq 160$ K in some ZnO QWs: the excitation-intensity dependence of biexcitonic PL spectra and of nonlinear pump–probe spectra have been reported so far. Figure 17 gives such an example taken for the MQW (Mg concentration $x = 0.27$ and 37 Å) at 5 K. We would like here to emphasize that the threshold for the biexciton recombination or formation is significantly lower than that for the x–x recombination, i.e., the biexcitonic gain is more advantageous from the viewpoint of the application as a low-threshold semiconductor laser. The three traces in figure 17 show the normalized PL spectra at various excitation powers under the optical excitation using a pulsed-dye laser (341 nm) [61]. At the lowest power density (0.1 kW cm$^{-2}$, figure 17(b)), the luminescence spectrum is dominated by radiative recombination of localized excitons (open circle, X). As the excitation power density increases, there appears a shoulder (a closed circle, XX) on the low-energy side of the X-band. This emission band, located at 3.35 eV, grows superlinearly with respect to the excitation intensity. With further increase in excitation intensity, a second peak denoted by P appears at around 3.32 eV. This assignment is supported by the rate-equation analysis for the dependence of biexciton PL intensity on the excitation density (cf figure 3 of [61]).

Probably because of the competition with the inelastic scattering process, stimulated emission related to the biexciton decay has not yet been observed experimentally.

6.3.2. Some other nonlinear spectroscopy and biexciton binding energy. In this subsection we deal with the experimental results of a nonlinear spectroscopic method and the conclusions which may be drawn from these results concerning biexcitons. The method discussed here is a two-step absorption into the biexciton states via really excited intermediate states of excitons.

In order to exploit the biexciton creation via the stepwise two-photon absorption and determine its binding energy, Chia et al [50] adopted a pump–probe transmission spectroscopy, in which a strong pump beam creates the high-density excitonic gas while a weak tunable beam probes the changes of the excitonic absorption. In their experiments, a ZnO MQW is illuminated by a XeCl excimer-laser beam and a second broad-band light source prepared by a dye solution. The use of the laser beam exactly tuned to the resonance simplifies the situation and the interpretation of the spectroscopic data. Under the condition of nonresonant excitation, the densely distributed electron–hole pairs initially created are very rapidly relaxed to exciton states, they surely also observed such induced absorption (cf figure 18). Moreover, they demonstrated that the transition involved in the induced
absorption process is from free-excitonic states to free-biexcitonic states even in the case of ZnO quantum structures where the localization effects are not negligible. Therefore, this experimental method is found to be useful to precisely determine the binding energy of biexcitons unlike the PL or stimulated emission spectroscopy. In the latter case, as already stated in subsection 6.1, the spectra are dominated by the radiative recombination of biexcitons localized at the potential variation caused by well width and depth fluctuations. No quantitative interpretation of these experiments has been performed yet. For small broadening, free biexciton binding energy can be estimated by using the energy separation between the exciton resonance and the lower-energy induced absorption process from free-excitonic states to free-excitonic states. Experimental results to provide definite evidence of the room-temperature biexcitonic gain are highly desirable by optimizing the QW design.

6.4. Electron–hole plasma

In this section we mention very briefly the electron–hole plasmas which have been used as a recombination process for the laser action of all semiconductor lasers commercially available. The basic physics is analogous to the case of one-component plasmas that are distributed inside a modulation-doped semiconductor. Such an emission (usually called N emission) has been observed in ZnO thin films and QWs at elevated pumping levels more intense than the case of x–x scattering. The QWs grown by a plasma-assisted MBE technique have exhibited only stimulated emission originating from the EHP phase. The EHP recombination process is also observed in the optical gain spectra. The peak value of this optical gain was estimated to be \( \simeq 390 \text{ cm}^{-1} \) at room temperature [62].

7. Conclusions

We have given an overview of the main linear and nonlinear optical properties of excitons in ZnO-based QWs. The fundamental importance of strongly bound excitons in terms of localization of excitons, temporal dynamics and oscillator strength has been addressed through the discussion of recent spectroscopic experiments. We also reported on the influence of an internal electric field present along the growth axis of wurtzite semiconductor QWs, resulting in the observation of PL of spatially separated electron–hole pairs due to the quantum-confined Stark effects in ZnO/MgO MQWs. The role of excitons in the operation of optoelectronic devices operating in the blue–ultraviolet regions has been emphasized in the discussion of the nonlinear optical properties. The unique combination of large exciton binding energy and reduced screening and phonon coupling occurring in QWs permit the observation of novel phenomena connected with the coexistence of exciton gas and free carrier gas at high density. This property is propitious to the stabilization of excitons at high temperatures. The confinement-induced enhancement of the exciton as well as biexciton binding energies were
demonstrated in QWs. Besides their fundamental importance, these phenomena are found to play an important role in the physics of blue–ultraviolet lasers and modulators.

Such high-quality MQWs open up numerous possibilities for UV optoelectric devices.

Acknowledgments

The quantum wells used as the target of optical characterization in our study were produced by Dr A Ohtomo and Dr K Tamura using equipment originally constructed by Dr Y Matsumoto, Tokyo Institute of Technology, Japan. We would like to express our gratitude to the above mentioned researchers, as well as Dr Nguyen Tien Tuan, Dr H D Sun, and Dr C H Chia, Institute of Physical and Chemical Research, Japan, for their assistance in all aspects of our research.

References

[1] Makino T, Chia C H, Tuan N T, Segawa Y, Kawasaki M, Ohtomo A, Tamura K and Koinuma H 2000 Appl. Phys. Lett. 76 3549
[2] Chen Y F, Ko H K, Hong S and Yao T 2000 J. Appl. Phys. 97 1624
[3] Hoffman R L, Norris B J and Wagner J F 2000 Appl. Phys. Lett. 76 82
[4] Segawa Y, Ohtomo A, Kawasaki M, Koinuma H, Tang Z, Yu P and Wongsiri G 1997 Phys. Status Solidi b 202 609
[5] Nomura K, Ohta H, Ueda K, Kamiya T, Hirano M and Nomura K, Ohta H, Ueda K, Kamiya T, Hirano M and
[6] Carcia P F, Mclean R S, Reilly M H and Nunes G 2003 Phys. Rev. Lett. 89 1122
[7] Nishii J, Hossain F M, Takagi S, Aita T, Saikusa K, Ohmaki Y, Ohkubo I, Kishimoto S and Ohtomo A 2003 Japan J. Appl. Phys. 42 L347
[8] Masuda S, Kitamura K, Okumura Y, Miyatake S, Tabata H and Kawai T 2003 J. Appl. Phys. 93 1624
[9] Hoffman R L, Norris B J and Wagner J F 2000 Appl. Phys. Lett. 85 733
[10] Mollwo E 1982 Semiconductor Physics of H–VI and I–VII Compounds, Semimagnetic Semiconductors (Landolt–Börnstein New Series) vol 17 ed O Madelung, M Schulz and H Weiss (Berlin: Springer) p 35
[11] Sun H D, Makino T, Tuan N T, Segawa Y, Tang Z K, Wong G K L, Kawasaki M, Ohtomo A, Tamura K and Koinuma H 2000 Appl. Phys. Lett. 77 4250
[12] Sun H D, Makino T, Segawa Y, Kawasaki M, Ohtomo A, Tamura K and Koinuma H 2002 J. Appl. Phys. 91 1993
[13] Sun H D, Makino T, Tuan N T, Segawa Y, Kawasaki M, Ohtomo A, Tamura K and Koinuma H 2001 Appl. Phys. Lett. 78 2464
[14] Makino T, Tuan N T, Sun H D, Chia C H, Segawa Y, Kawasaki M, Ohtomo A, Tamura K and Koinuma H 2000 Appl. Phys. Lett. 77 975
[15] Bernardini F, Fiorentini V and Vanderbilt D 1997 Phys. Rev. Lett. 79 3958
[16] Park S-H and Chuang S-L 2000 J. Appl. Phys. 87 353
[17] Cingolani R, Larocca G, Kalt H, Ploog K and Mann J 1991 Phys. Rev. B 43 9662
[18] Langer R, Simon J, Ortiz V, Pelekanos N T, Barski A, Andre R and Godlewski M 1999 Appl. Phys. Lett. 74 3827
[19] Leroux M, Grandjean N, Laugt M, Massies J, Gil B, Lefebvre P and Bingenfeld P 1998 Phys. Rev. B 58 R13371
[20] Krishnamurthy S, Iladis A A, Inampudi A, Choopun S, Vispute R D and Venkatesan T 2002 Solid State Electron. 46 1633
[21] Makino T, Segawa Y, Kawasaki M, Ohtomo A, Shiroki R, Tamura K, Yasuda T and Koinuma H 2001 Appl. Phys. Lett. 78 1237
[22] Kawasaki M, Ohtomo A, Shiroki R, Ohkubo I, Kimura H, Isoya G, Yasuda T, Segawa Y and Koinuma H 1998 Extended Abstracts of the 1998 Int. Conf. on Solid State Devices and Materials (Hiroshima: Business Ctr. Acad. Soc. Japan) p 356
[23] Vispute R D et al 1998 Appl. Phys. Lett. 73 348
[24] Narayan J, Dovidenko K, Sharma A K and Oktyabrsky S 1998 J. Appl. Phys. 84 2597
[25] Ohkubo I et al 2002 J. Appl. Phys. 92 5587
[26] Edahiro T, Fujimura N and Ito T 2003 J. Appl. Phys. 93 7673
[27] Bogata V, Goldenblum A, Many A and Goldstein Y 1999 Phys. Status Solidi b 212 39
[28] Chen Y, Ko H, Hong S, Sekiuchi T, Yao T and Segawa Y 2000 J. Vac. Sci. Technol. B 18 1514
[29] Matsumoto Y, Murakami M, Jin Z W, Ohtomo A, Lippmaa M, Kawasaki M and Koinuma H 1999 Japan J. Appl. Phys. Part 2 38 L603
[30] Coli G and Bajaj K K 2001 Appl. Phys. Lett. 78 2861
[31] Ohtomo A, Kawasaki M, Ohkubo I, Koinuma H, Yasuda T and Segawa Y 1999 Appl. Phys. Lett. 75 980
[32] Pollmann J and Böttner H 1977 Phys. Rev. B 16 4480
[33] Schwarz R B, Khachatryan K and Weber E R 1997 Appl. Phys. Lett. 70 1122
[34] Giergens L, Ambacher O, Stutzmann M, Miskys C, Scholz F and Off J 2000 Appl. Phys. Lett. 76 577
[35] Bykhovskii A, Gelmont B and Shur M 1993 J. Appl. Phys. 74 6734
[36] Makino T, Isoya G, Segawa Y, Chia C H, Yasuda T, Kawasaki M, Ohtomo A, Tamura K and Koinuma H 2000 J. Cryst. Growth 214–215 289
[37] Ohtomo A, Shiroki R, Ohkubo I, Koinuma H and Kawasaki M 1999 Appl. Phys. Lett. 75 4088
[38] Cingolani R 1997 Optical Properties of Excitons in ZnSe Based Quantum Well Heterostructures vol 44 (San Diego, LA: Academic) chapter 3, p 163
[39] Duke C B and Mahan G D 1965 Phys. Rev. 139 A 1965
[40] Rudin S, Reinecke T L and Segall B 1990 Phys. Rev. B 42 11218
[41] Pelekanos N T, Ding J, Hagerott M, Nurmiikko A V, Luo H, Samarth N and Furdyna J K 1992 Phys. Rev. B 45 6037
[42] Alperovich V L, Zaletin V M, kravchenko A F and Terekhov A S 1976 Phys. Status Solidi b 77 465
[43] Fischer A J et al 1994 Phys. Rev. Lett. 73 2368
[44] Lee D, Johnson A M, Zucker J E, Feldman R D and Austin R F 1991 J. Appl. Phys. 69 6722
[45] Zhang X B, Taliercio T, Koliakos S and Lefebvre P 2001 J. Phys.: Condens. Matter 13 7053
[46] Goni A R, Cantareo A, Syassen K and Cardona M 1990 Phys. Rev. B 41 10111
[47] Gurioli M, Martínez-Pastor J, Colocci M, Bosacchi A, Franchi S and Andreani L C 1993 Phys. Rev. B 47 15755
[48] Shinada M and Sagano S 1966 J. Phys. Soc. Japan 21 1936
[49] Gourdon C and Lavallard P 1989 Phys. Status Solidi b 153 641
[50] Chia C H, Makino T, Segawa Y, Kawasaki M, Ohtomo A, Tamura K and Koinuma H 2001 Appl. Phys. Lett. 90 3650
[51] Segall B and Mahan G D 1968 Phys. Rev. Lett. 171 935
[52] Gross E, Fermorogov S and Razbirin B 1966 J. Phys. Chem. Solids 27 1647
[53] Weis R L and Tait W C 1968 Phys. Rev. 166 791
[54] Makino T, Tamura K, Chia C H, Segawa Y, Kawasaki M, Ohtomo A and Koinuma H 2002 Appl. Phys. Lett. 81 2355
[55] Makino T, Tamura K, Chia C H, Segawa Y, Kawasaki M, Ohtomo A and Koinuma H 2002 Phys. Rev. B 66 233305
[56] Kaliakas S, Zhang X B, Taliercio T, Lefebvre P, Gil B, Grandjean N, Damilano B and Massies J 2002 Appl. Phys. Lett. 80 428
[57] Hopfield J J 1958 Phys. Rev. 112 1555
[58] à la Guillaume C B, Debever J M and Salvan F 1969 Phys. Rev. 177 567
[59] Ohtomo A, Tamura K, Kawasaki M, Makino T, Segawa Y, Tang Z K, Wong G, Matsumoto Y and Koinuma H 2000 Appl. Phys. Lett. 77 2204
[60] Ohtomo A 2000 Quantum structures and ultraviolet light-emitting devices based on ZnO thin films grown by laser molecular-beam epitaxy PhD Thesis Tokyo Institute of Technology
[61] Sun H D, Makino T, Segawa Y, Kawasaki M, Ohtomo A, Tamura K and Koinuma H 2001 Appl. Phys. Lett. 78 3385
[62] Makino T, Sun H, Nguyen T T, Segawa Y, Chia C, Kawasaki M, Ohtomo A, Tamura K and Koinuma H 2001 Proc. of the 2nd Int. Conf. on Combinatorial and Composition Spread Techniques in Material and Device Development (San Jose) USA vol 4281 ed G Jabbour and H Koinuma (Bellingham, WA: SPIE) p 68
[63] Hvam J M 1973 Solid State Commun. 12 95