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Strain effects on exciton resonance energies of ZnO epitaxial layers

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Magnitudes of strain in ZnO epitaxial layers grown on sapphire(0001) substrates under various growth conditions were experimentally determined by x-ray diffraction. We discuss the strain-induced energy shift on the exciton resonances, the results of which were analyzed theoretically using the Hamiltonian for the valence bands under in-plane biaxial strain. Comparative studies with GaN evidenced the advantages of ZnO in terms of sensitivity of the strain-induced energy shift and of piezoelectric effect in heterostructures. © 2001 American Institute of Physics. [DOI: 10.1063/1.1398328]

Much effort has recently been devoted to the studies on ZnO epitaxy due to the potential application as semiconductor laser diodes. This wide-gap semiconductor ensures an excitonic effect, which can be utilized at temperatures well above room temperature.^{1–3} Therefore, a lower pumping threshold for the gain emergence can be expected, in principle, if an exciton-related recombination rather than an electron-hole plasma recombination is used. An example of the latter is an $\text{In}_x\text{Ga}_{1-x}\text{N}$ laser.⁴ ZnO epilayers oriented in the c -axis direction suffer from biaxial strain due to the mismatch of lattice constants between the epilayer and the substrate. Quantum well (QW) structures also suffer from a certain amount of strain. These strains may induce, for example, the formation of dark-line defects and a piezoelectric effect as discussed in the studies on ZnSe or GaN optoelectric devices. These defects tend to shorten the operational lifetime of the device, while the piezoelectric effect can lead to a reduction in the oscillator strength for excitonic transition. It should be noted that since the stimulated emission and/or laser action in ZnO related materials are of excitonic origin, the strain never becomes advantageous for reducing the gain threshold.

The in-plane lattice constant of sapphire(0001) substrate is largely mismatched with that of ZnO (18%). However, the actual amount of strain depends on the epitaxy mechanism and hence growth conditions, e.g., growth and annealing temperatures. It is important to achieve deeper understanding of the electronic structures of ZnO under in-plane biaxial strain, in particular, the strain dependencies of the exciton resonance energies.

In this letter, we present the optical properties of strained ZnO epilayers. The exciton resonance energies were esti-

mated as a function of strain. These experimental results were analyzed using the strain Hamiltonian.

The samples were nominally undoped submicron-thick ZnO(0001) epilayers, which were grown on sapphire(0001) substrates by laser molecular-beam epitaxy. To control the lattice strain systematically, we used various types of samples at various growth and annealing temperatures. Reflection spectra were taken at 4.2 K using a xenon lamp as an excitation source. The spectral resolution was 1.5 meV.

Figures 1(a) and 1(b) show the annealing temperature dependence of the lattice constants of c and a axes in two typical ZnO epilayers and the relationship between c - and a -lattice constants, respectively. These were measured using the four-axis x-ray diffraction. The residual strain along the a - and c -axes were estimated by $\epsilon_{xx} = (a - a_0)/a_0$ and $\epsilon_{zz} = (c - c_0)/c_0$, where a_0 and c_0 are, respectively, the lattice constants in the unstrained crystal and taken as $a_0 = 3.2505$ and 5.2048 Å. Since there is the relationship of $\epsilon_{zz} = -2(C_{13}/C_{33})\epsilon_{xx}$ (in-plane biaxial strain), we define the Poisson ratio as $\nu = C_{13}/C_{33}$. Here, C_{i3} ($i = 1-3$) denote the components of the elastic stiffness constants. One can deduce, $\nu \approx 0.5$ from the fitting shown in Fig. 1(b). Our estimated value is closer to that obtained in a bulk⁵ ($\nu = 0.50$) rather than that in a sputtered film⁵ ($\nu = 0.40$).

Figure 2 shows a reflection spectrum in a strained ZnO taken at 4.2 K. Three transitions labeled “A,” “B,” and “C,” which correspond to transitions from respective valence bands to the conduction band, can be seen. In Wurtzite-type II–IV compounds, three exciton series (A, B, and C) that are formed from the s -like (Γ_{7c}) conduction band and the three p -like (Γ_{7v}^u , Γ_{9v} , and Γ_{7v}^l) valence bands (cf. inset of Fig. 2), are observed.^{6,7} A and B transitions are allowed for light polarization perpendicular to the c axis, while the C transition is essentially allowed for polarization parallel to the c axis. Because of the c -axis orientation, A and B transitions are dominant.

The resonance energies (E_A and E_B) were summarized in Fig. 3 as functions of strain, ϵ_{zz} (strain parallel to the c

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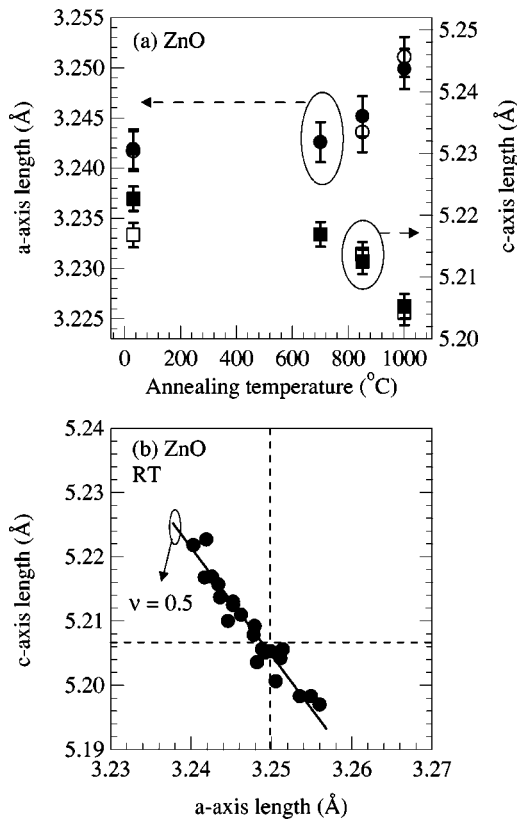


FIG. 1. (a) Annealing temperature dependences of lattice constants of *a* (open and closed circles) and *c* axes (open and closed squares) for two representative samples of ZnO epilayers are shown. (b) Length of *c* axis is plotted against the length of *a* axis for the films under various growth and annealing conditions. The solid line corresponds to the fitted results. The lattice constants of unstrained ZnO are shown by dashed lines.

axis). The fitting results reported for GaN layers are also plotted.⁸ Energies of E_A and E_B are both linearly increasing functions of strain. The exciton energies of GaN shows a complicated and nonlinear behavior on strain. Inhomogeneity of the strain inside the epilayers or QWs induces an inhomogeneous broadening of energy distribution of the exciton states in GaN. Such a strain insensitivity inherent to ZnO conserves the width of exciton energy states even if the strain distributes inhomogeneously inside the samples. We now consider the reason of this difference in the strain dependence.

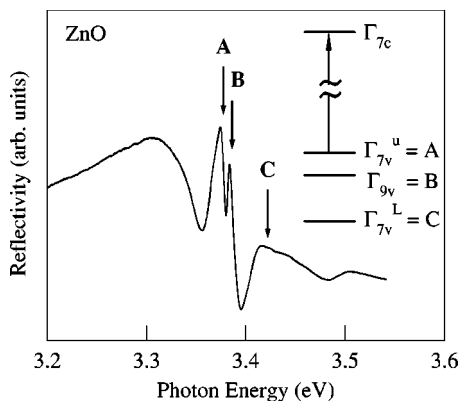


FIG. 2. Typical reflectance spectrum of ZnO/sapphire epilayers measured at 4.2 K is shown. Structures labeled “A,” “B,” and “C” are due to resonances of A, B, and C excitons, respectively. Inset is the band diagram of ZnO.

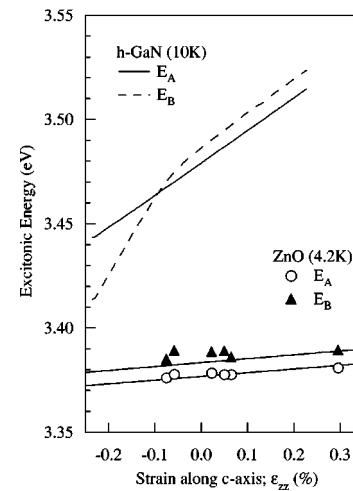


FIG. 3. Exciton resonance energies, E_A (○) and E_B (▲), as functions of ϵ_{zz} are shown. Quantity of ϵ_{zz} represents the uniaxial strain along the *c* axis, which is plus for tensile (biaxially compressive) strain. Theoretically fitted lines are also shown. The excitonic resonance energies in unstrained crystal [E_A^0 and E_B^0] are 3.3775 eV and 3.3875 eV, respectively. Theoretically fitted results for hexagonal GaN epilayers at 10 K (Ref. 8) are also plotted by solid and dashed curves for comparison.

For this purpose, we fit the experimental results with the equations derived by Rowe *et al.*⁹ The equations for the strain dependence have been obtained from the strain Hamiltonian.^{10,11} Keeping only terms up to the second order in the strain and within a cubic approximation, the energies for A and B exciton states are

$$E_A^1 = E_A^0 + \delta_1 + \alpha_+ \delta_2 - \alpha_+ \alpha_- \delta_2^2 / (E_C^0 - E_A^0), \quad (1)$$

$$E_B^1 = E_B^0 + \delta_1 + \delta_2, \quad (2)$$

where $\delta_1 = (D_1 - D_2/\nu)\epsilon_{zz}$, $\delta_2 = (D_3 - D_4/\nu)\epsilon_{zz}^2$, and $2\alpha_{\pm} = 1 \pm [(\Delta_1 - \Delta_2)[(\Delta_1 - \Delta_2)^2 + 8\Delta_2^2]^{-1/2}$, with E_i^j ($i = A-C$ and $j = 0,1$) are the resonance energies for these three exciton states in unstrained and strained cases. D_i ($i = 1-4$) and ν are deformation potential constants and the earlier-mentioned Poisson ratio, respectively. Quantities Δ_1 and $3\Delta_2$ are crystal-field and spin-orbit splittings, respectively. The difference in the strain dependence between ZnO and GaN is attributed to the difference in the magnitude of the proportional coefficient of the fourth term of Eq. (1), especially “ $\alpha_+ \alpha_-$.” Note, symmetries of these valence bands (“valence band ordering”)¹² are reversed between ZnO and GaN due to the negative spin-orbit splitting.¹³ Table I shows the values¹⁴ of Δ_1 , Δ_2 , and $\alpha_+ \alpha_-$ where $\alpha_+ \alpha_-$ of GaN is 38 times of magnitude larger than that of ZnO. The difference in the sign between Δ_1 and Δ_2 in ZnO results in the smaller value of $\alpha_+ \alpha_-$. We obtained the following parameters: $D_1 - D_2/\nu = 167$ and $D_3 - D_4/\nu = -166$.

TABLE I. Crystal-field (Δ_1), spin-orbit splitting related energies (Δ_2), and $\alpha_+ \alpha_-$ in Eq. (1) of ZnO and GaN are shown.

Material	Δ_1	Δ_2	$\alpha_+ \alpha_-$
ZnO ^a	40.8 meV	-1.57 meV	2.71×10^{-3}
GaN ^b	22 meV	5 meV	1.0×10^{-1}

^aFrom Ref. 14.

^bFrom Ref. 8.

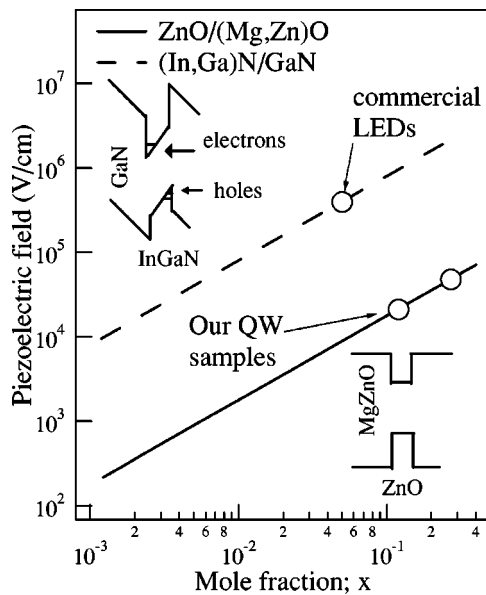


FIG. 4. Magnitude of a piezoelectric field by the mismatch-induced strain in QWs as a function of mole fraction, x , in $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ (dashed line) and $\text{ZnO}/\text{Mg}_x\text{Zn}_{1-x}\text{O}$ (solid line) QWs is shown. The Mg mole fractions of QWs targeted in our previous study (Ref. 22) and In concentration of a commercial light-emitting diode (Ref. 23) are shown by open circles. The data for $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ are from Refs. 16, 17, and 19. Inset shows schematic band diagram of ZnO QWs (right-hand side bottom) and of InGaN QWs under the piezoelectric field (left-hand side top, cited from Ref. 24). Electrons and holes distributed in the InGaN well regions are spatially separated due to the well-known quantum-confined Stark effects.

We now evaluate the magnitude of strain generated between the barrier and well layers when a QW structure is constructed. A (Zn,Mg)O alloy is considered to be a suitable material as a barrier due to its wider band gap¹⁵. Wurtzite crystals may generate piezoelectric fields when subject to external stress due to a biaxial strain-induced polarization, which is expressed by¹⁶ $P_z = 2d_{31}(C_{11} + C_{12} - 2C_{13}^2/C_{33})\epsilon_{xx}$, where d_{31} is the piezoelectric constant, C_{ij} are the elastic constants, and ϵ_{xx} is the in-plane strain. Figure 4 shows the magnitude of a piezoelectric field induced by the strain in QWs as a function of mole fraction, x , in $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ and $\text{ZnO}/\text{Mg}_x\text{Zn}_{1-x}\text{O}$ QWs. Here, piezoelectric strain coefficients of $d_{31} \approx -0.9 \times 10^{-10}$ cm/V for GaN and $d_{31} \approx -5 \times 10^{-10}$ cm/V for ZnO were used.^{17,5} The concentration dependences of lattice constants for both QWs were from Refs. 16, 18, and 19. The piezoelectric field effect become negligibly problematic in the case of ZnO unlike that in the case of GaN. Small lattice mismatch between ZnO and ZnMgO is surely responsible for this small piezoelectric field. Such a piezoelectric field may lead to spatial separation of the electrons and holes distributed in the well layer region and hence to the reduction of the oscillator strength for the excitonic transition. The combination of a (Mg,Zn)O barrier and ZnO well is, however, advantageous in terms of lattice-mismatch-induced strain compared to InGaN/GaN QWs. In addition, by adopting the combination of a MgZnO barrier and CdZnO well, we can attain perfectly in-plane lattice-matched QWs.^{20,21} This is because, as revealed in our previous study (see Fig. 3 in Ref. 20), the relationship in the a -lattice constant between Mg and Cd concentrations (x and y), in which the perfectly lattice-matching conditions are attained, is given by: $x = 0.0556 + 3.98y - 4.09y^2$.

In summary, the growth condition dependence of strain in ZnO epilayers on sapphire(0001) substrates was experimentally estimated by determining the lattice constants with an x-ray diffraction technique. Exciton resonance energies were experimentally determined as functions of strain by measuring the reflection spectra 4.2 K. The excitonic energies in ZnO are insensitive to the influence of strain compared with those in GaN. We described the advantage of ZnO/MgZnO and CdZnO/MgZnO QWs in terms of small strain (i.e., piezoelectric field), which is compared to the case of GaN-related QWs.

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