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Influence of composition diffusion on the band structures of InGaNAs/GaAs quantum wells investigated by the band-anticrossing model

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We investigate the influence of quantum-well intermixing (QWI) on the electronic band structure of GaInNAs/GaAs multiquantum wells. The band structures and optical transitions have been calculated based on the band-anticrossing (BAC) model and Fick's interdiffusion law for both intermixed and nonintermixed samples, respectively. The calculated results are consistent with the true optical transitions observed by photoluminescence excitation spectroscopy and secondary ion mass spectroscopy. Our investigation indicates that BAC model is valid for interdiffused quantum wells and verifies that the QWI process in GaInNAs/GaAs multiquantum wells is induced mainly by the interdiffusion of In–Ga between the quantum wells and barriers. © 2005 American Institute of Physics. [DOI: 10.1063/1.2138350]

Recent research has found that due to the interaction between localized N and GaInAs quantum well states, the GaInNAs/GaAs quantum well alloy semiconductor structure possesses better electron confinement and temperature stability. Consequently, its possibility of long wavelength emission and uncooled laser devices application^{1–3} are attractive advantages. Moreover, GaInNAs can be either lattice matched or pseudomorphically grown on GaAs, which allows fabrication of advanced devices including vertical cavity surface emission lasers^{4–6} and vertical cavity semiconductor optical amplifiers.^{7,8}

For many applications, achieving multiband gap functionality from a single substrate is essential, and quantum-well intermixing (QWI) in GaInNAs related materials⁹ has been demonstrated for this purpose. Understanding the influence of QWI on the electronic band structure is therefore crucial for extending the application of the GaInNAs/GaAs materials system. Chan *et al.* have calculated the band structure of intermixed GaInNAs/GaAs quantum wells (QWs) by using a traditional effective mass theory.¹⁰ However, in dilute nitrides, the band anticrossing (BAC) model, which emphasizes the intrinsic interaction between the localized N and InGaAs/GaAs quantum well states,^{11,12} has proven to be a more effective model. In this letter, we calculate the electronic structures in intermixed and nonintermixed samples based on the BAC model and Fick's diffusion law describing the group III elements diffusion. The calculated optical transitions have been compared with experimental observation by photoluminescence excitation (PLE) spectra.

The samples used in this study are molecular beam epitaxy grown 5 periods Ga_{0.62}In_{0.38}N_{0.015}As_{0.985}/GaAs quantum well, with 7 nm well width and 30 nm barrier width. As-grown samples were *in situ* annealed at 750 °C to activate efficient luminescence. This annealing process ensured the blueshift saturation as demonstrated by the negligible additional blueshift under further annealing. Subsequent selective QWI has been achieved by means of rapid thermal annealing combined with depositing SiO₂-cap layers by different techniques, namely sputtering and plasma-enhanced chemical vapour deposition. Details about the sample growth and processing can be found elsewhere.¹⁰ Here, we focus on the comparison of the optical transitions between two samples, one of which is intermixed and the other is nonintermixed.

Figure 1 shows the PLE spectra of two such samples, which clearly demonstrates the change of the optical transitions before and after intermixing by sputtering 50-nm-thick SiO₂ capping layer and annealing at 700 °C for 180 s. It has been pointed out that the measurement of the PL spectrum, which only presents material ground states, is insufficient for the accurate description of interdiffusion processes because the excited states are more sensitive to the changes of QW

FIG. 1. PLE spectra of nonintermixed (upper) and intermixed (lower) samples at 10 K. The calculated optical transitions are marked in the spectra.

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FIG. 2. Calculated transition energies as a function of coupling strength for the nonintermixed QWs.

profile.¹³ Conversely, PLE spectra containing several optical transitions faithfully represent the influence of QW potential profile on the quantized states; therefore the fitting of such multiple transitions provides more complete characterization of the diffusion process.

The calculation of the band structure of both intermixed and nonintermixed samples is based on BAC model, which describes the coupling between localized N states and GaInAs extended states. It can be solved by extracting the eigenvalue of the two band Hamiltonian^{11,12}

$$H = \begin{pmatrix} E_M(x, z) + \frac{\hbar^2 k^2}{2m_e} & V_{MN}(x, z) \\ V_{MN}(x, z) & E_N(x, z) \end{pmatrix}, \quad (1)$$

where

$$E_M(x, z) = \begin{cases} E_{C\text{InGaAs}}(z) - 1.55y & z \leq |a| \\ E_{C\text{Barrier}}(z) & z > a, \end{cases} \quad (2)$$

$$V_{MN} = \beta\sqrt{y} \quad \beta = \begin{cases} 1.6-3.0 & z \leq |a| \\ 0 & z > a. \end{cases} \quad (3)$$

$E_{C\text{InGaAs}}(z)$ is the conduction band edge of the material without nitrogen (InGaAs), which is a function of growth direction (z) due to the interdiffusion of the In composition along the well and barrier. Parameter y is the nitrogen concentration, which is 0.015 in this letter. V_{MN} is the coupling strength between N and InGaAs indicated by a constant coefficient β that is reported variously from 1.6 to 3.0.¹⁴

It is assumed that the diffusion in our samples is mainly contributed by group III atoms In and Ga. This assumption has been supported by secondary ion mass spectroscopy (SIMS) studies.⁹ The composition profile after interdiffusion is characterized by a diffusion length $L_d = (Dt)^{1/2}$, where D is defined in Fick's law as the diffusion coefficient and t is annealing time. For a GaInNAs/GaAs QW with In mole

FIG. 3. Calculated band structures of intermixed QWs with different diffusion length, in (a) conduction band, and (b) valence band.

fraction given by x_0 , the composition profile of In after interdiffusion can be described by an error function

$$x(z) = \frac{x_0}{2} \left[\text{erf}\left(\frac{L_z + 2z}{4L_d}\right) + \text{erf}\left(\frac{L_z - 2z}{4L_d}\right) \right], \quad (4)$$

where L_z is the as-grown well width, z is along the crystal growth direction, and the quantum well center is at $z=0$. Group III atom concentrations are functions of growth direction z which gradually change crossing the well and barrier but group V atoms, N (y) and As ($1-y$), are discontinuous in the interface which only exist in the quantum well. Depending on the alloy composition, the energy band gap of ternary alloy $\text{In}_{x(z)}\text{Ga}_{1-x(z)}\text{As}$ can be described using a quadratic expression¹⁵ including bowing terms which accounts for the deviation from a linear interpolation between two binary alloys. The other material parameters including lattice constant a , effective mass, Luttinger parameters, conduction band hydrostatic deformation potential a_c , and valence band hydrostatic deformation potential a_v , shear deformation potential b and, elastic stiffness constants C_{11} and C_{12} are calculated by interpolation of the binary parameters of InAs and GaAs. In order to include the N influence to strain, the GaN and InN lattice constants are also included in calculating the lattice constant with quaternary form and all the material parameters are adopted from Ref. 15.

Due to the high strain of the $\text{Ga}_{0.62}\text{In}_{0.38}\text{N}_{0.015}\text{As}_{0.985}/\text{GaAs}$ quantum wells considered here, it is crucial to consider coupling between the heavy hole (HH), light hole (LH) and SO bands, therefore we adopt the 6×6 Hamiltonian in calculating valence band.¹⁶ The parameters are consistent with Ref. 16. As the strain is compressive, the hydrostatic component $H_{c,v}(z)$ will broaden the band gap and the shear component $S_v(z)$ will enlarge the splitting between the HH and LH at band edge $k=0$.

We start with fitting the nonintermixed QWs to confirm the coupling parameter β to be used in the BAC model, which is determined by the wave function overlap between N and InGaAs/GaAs. Because from the SIMS study, it is found that N concentration is the same in two samples, we assume the magnitude of β is constant before and after intermixing by considering the average interaction in a mixture environment of N neighbor environment.¹⁷ We calculate the transition energies (at 10 K temperature) with varying β from 2.0 to 2.4 to fit the experimental results. The dependence of different transition energies on the coupling strength is shown in Fig. 2, which shows that due to the large bowing induced by localized N, the band gap will shrink at a rate of

FIG. 4. Dependence of calculated optical transition energies on diffusion length.

$-1.11 \text{ eV}/(+1\beta)$ with increase of interaction strength. Through the comparison with experimental results, it is clearly seen that all three optical transitions $E_1\text{-HH}_1$, $E_1\text{-LH}_1$, and $E_2\text{-HH}_2$ are in good agreement with experimental values when β is chosen as 2.1, which assures the validity of the parameter selection and our fitting process.

Then we calculate the transition energies in the diffused sample with various diffusion lengths. With $\beta=2.1$ in the BAC model, the band structure with different diffusion lengths in the quantum well is illustrated in Fig. 3, which shows that the fundamental band edge lifts while high order states energies decrease due to the widening of well width with increase of diffusion length. The energy levels of the light-hole states are determined by the interplay of strain and well width effects. With an increase in the diffusion length, the concentration of In composition in the QW decreases, causing a decrease of the compressive strain. Therefore the hydrostatic component of electrons and holes will be decreased, which shrinks the splitting of conduction and valence band edge, although the consequent widening of the InGaAs/GaAs band gap will diminish this effect. Meanwhile, the shear component determining the degeneracy of HH and LH is reduced. These three processes, the hydrostatic component shift of band gap, the increase of InGaAs/GaAs band gap and the shear component lifting the degeneracy of the valence band, complete to decide the energy of the quantized states.

With the same coupling strength, the transition energies between different quantized levels change with the diffusion lengths are shown in Fig. 4. We observe that the transition energies change sharply in the region of 0.5–5 nm of diffusion lengths for the group III atoms. This illustrates the competition between the three processes described earlier. By comparing with the experimental PLE spectra the diffusion length is determined to be 7.5 nm. The calculated transitions of $E_1\text{-HH}_1$, $E_1\text{-LH}_1$, and $E_2\text{-HH}_2$ in this case are marked in the PLE spectrum of the interdiffused sample in Fig. 1. By

fitting the In composition profile determined by SIMS, the experimentally estimated diffusion length is $\sim 6.1 \text{ nm}$. The theoretical estimation can be considered in reasonably consistent with experiment if the composition error induced by ion beam mixing effect and the inaccuracy of the transition energies derived from PLE spectrum are taken into account. In addition, the calculated result show that transition energies are not very sensitive to the diffusion length when $L_d > 5.5 \text{ nm}$. Therefore, the earlier-mentioned error should not overrule the validity of our model. The agreement between the theory and experiment implies the validity of the BAC model for interdiffused QWs. In addition, as the diffusion mechanism strongly influences the strain distribution¹⁸ and thus the energy separation between $E_1\text{-HH}_1$ and $E_1\text{-LH}_1$, our investigation verifies the assertion that the compositional diffusion in GaInNAs/GaAs QWs mainly occurs in the group III elements In and Ga.

In conclusion, with the combination of Fick's law and the band-anticrossing model, the effect of compositional interdiffusion in GaInNAs/GaAs quantum well on the electronic structure has been investigated. Theoretical calculation of multiple transition energies is in agreement with PLE and SIMS measurement results. Our investigation indicates the validity of BAC model for describing the electronic structures in dilute nitride QWs with disordered composition as well as verifying that interdiffusion of group III elements In and Ga is the main mechanism responsible for quantum-well intermixing.

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