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JOURNAL OF APPLIED PHYSICS **101**, 123515 (2007)

Deep-level emissions in GaAsN/GaAs structures grown by metal organic chemical vapor deposition

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This work presents the deep-level photoluminescence of coherently strained GaAsN/GaAs quantum-well (QW) structures with various GaAsN thicknesses and N contents. A broad deep-level emission at ~1.1 eV is observed, whose wavelength is redshifted as the GaAsN thickness increases. Based on its energy separation from the QW emission, this emission is attributed to a transition between the QW electron ground state and a deep level at ~0.2 eV above the GaAsN valence-band (VB) edge. This level is shown to be tied to the GaAs band edge. A transition between this level and the GaAs conduction band allows the GaAsN–GaAs band alignment to be evaluated. A type II band lineup is obtained with VB offsets of 0.03 and 0.002 eV for N=0.6% and 1.8%, respectively. The decreased VB offset suggests a transition from type II to type I with increasing N content. Thermal annealing effectively removes this level and improves the QW emission. The concentration of this level is not clearly correlated with N content, suggesting that this level is induced by a low-temperature growth of the GaAsN layer to suppress the composition fluctuation. Given its energy, this level is tentatively assigned to V_{Ga}. *© 2007 American Institute of Physics.*
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I. INTRODUCTION

The large differences between both sizes and atomic orbital energies of the As and N atoms cause the GaAsN band gap to decrease considerably as the N content increases.[1–10] The optical bowing coefficient is very large and depends strongly on composition.[3–7] Wei and Zunger[6] have divided the GaAsN band gap into two regions: (i) a bandlike region in which the bowing coefficient is relatively small and (ii) an impuritylike region (dilute N) in which the bowing coefficient is larger and composition dependent. A controversy remains over whether the band alignment for dilute N is type I[10–12] or type II.[5,8,9] Experimental evaluation of the valence-band (VB) alignment is difficult because the experimental uncertainty often exceeds the very small VB offset.[8–12] Deep levels with their strongly localized wave functions can be used as probes of interfacial band structures.[13,14] However, the properties of the deep levels and their related emissions in this material system have seldom been reported.

This work investigates the deep-level emissions of the GaAsN/GaAs single-quantum-well (SQW) structures with various GaAsN thicknesses and N compositions. A prominent deep-level emission at ~1.1 eV which exhibits a quantum-size-confinement effect is presented here. The effects of temperature, excitation power, and postgrowth annealing on this emission are studied. Transitions that involve this level are analyzed to evaluate the GaAsN/GaAs band alignment. Moreover, the assignment of the 1.1 eV emission is discussed.

II. EXPERIMENTS

The GaAs/GaAsN/GaAs SQW samples were grown on n^{+}-GaAs (001) substrates by low-pressure metal organic chemical vapor deposition (MOCVD). The GaAsN layer was undoped to avoid the introduction of any unwanted shallow impurity states. This GaAsN layer was inserted between two 0.3 μm Si-doped GaAs layers with a concentration of 6×10^{16} cm^{-3} for electrical measurements. The GaAsN layers were grown at ~500 °C using dimethylhydrazine (DMHY) as a nitrogen source in combination with triethylgallium and AsH_3. Detailed growth conditions can be found elsewhere.[15] The N content was determined from double-crystal x-ray diffraction and verified with photoluminescence (PL) peak energy. None of the studied samples showed strain relaxation, according to their x-ray diffraction patterns which show clear interference fringes.[15] PL spectra were measured using an excitation of the 532 nm line from a solid-state laser.

III. MEASUREMENTS AND RESULTS

A. Thickness-dependence of the PL spectra

Figure 1 shows the 30 K PL spectra of the N=1.8% SQW samples with GaAsN thickness ranging from 40 to 250 Å. Each spectrum generally consists of two peaks. The high-energy peak originates from the GaAsN quantum states, as evidenced by the redshift of the emission energy with the increase in the GaAsN thickness. The line shape is quite symmetric without the previously reported low-energy tail,[16] suggesting no obvious compositional fluctuation. Lower growth temperatures of the GaAsN layer may suppress the compositional fluctuation but degrade optical properties due to the formation of recombination centers. In addition to the QW emission, a broad peak arises at the low-

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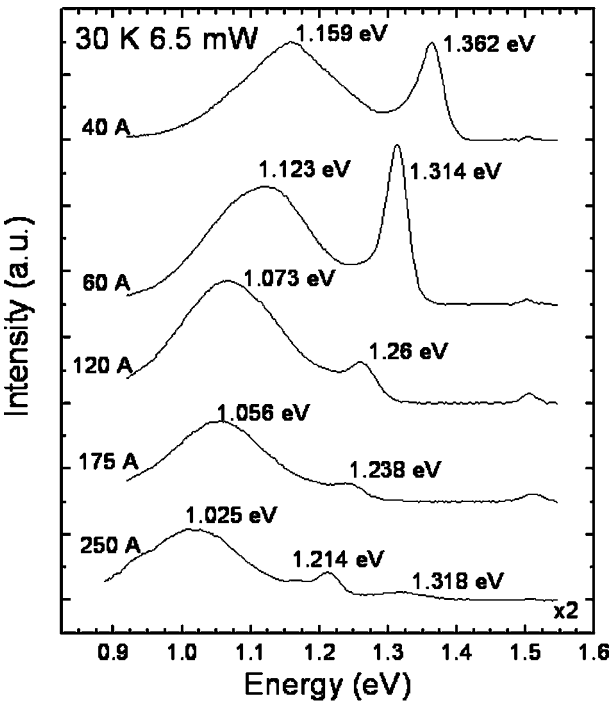

FIG. 1. 30 K PL spectra of the N=1.8% GaAsN/GaAs SQW samples with different GaAsN thicknesses at an excitation power of 6.5 mW. Besides the QW emission, each spectrum displays at the lower energy side a broad emission at ~1.1 eV, which is shifted along with the QW emission. The energy separation between this and the QW emissions is about 0.2 eV, suggesting that the 1.1 eV emission is a transition that involves the electron ground state in the well and a deep level state at about 0.2 eV above the GaAsN valence-band edge.

energy side. This peak is considered to originate from a deep level and is designated as "1.1 eV emission" because of the proximity of peak emission energies. Similar defect emissions have been reported[9,17,18] but no detailed properties. This deep-level emission displays a similar size-confinement effect as QW emission. The wavelength of the deep-level emission shifts from 1.159 to 1.028 eV as the GaAsN thickness increases from 40 to 250 Å. Notably, the energy separation between this and the QW emissions remains a constant ~0.2 eV.

Since a spatially indirect transition normally has a very small transition probability, the prominence of the 1.1 eV emission and its size-confinement effect indicate a strong spatial correlation between the corresponding deep level and the GaAsN well. Thus, the authors believe that the deep level is in or around the GaAsN well rather than in the GaAs substrate which is at least ~0.3 μm from the GaAsN well. Since the wave function for an electron that is trapped on a deep defect state is strongly localized, further confinement due to the well width is expected to be very weak. Thus, a reasonable explanation for the size-confinement effect is that the 1.1 eV emission must involve the ground state of the GaAsN well. Although controversy remains over whether the alignment is type I or II, the band gap bowing in GaAsN/GaAs (dilute N) is commonly accepted to be mainly in the conduction band (CB) with a very small VB offset.[8–12] Thus, the 1.1 eV emission is regarded as a transition between the QW electron ground state (EGS) and the deep level. The energy difference between the 1.1 eV and QW emissions is the energy location of this deep level relative to the GaAsN VB edge, which is at ~0.2 eV above the GaAsN VB edge. The 1.1 eV emission cannot be an indirect transition in real space between the QW EGS and the neighboring GaAs VB because if it were, the VB offset would be 0.2 eV which is too large.

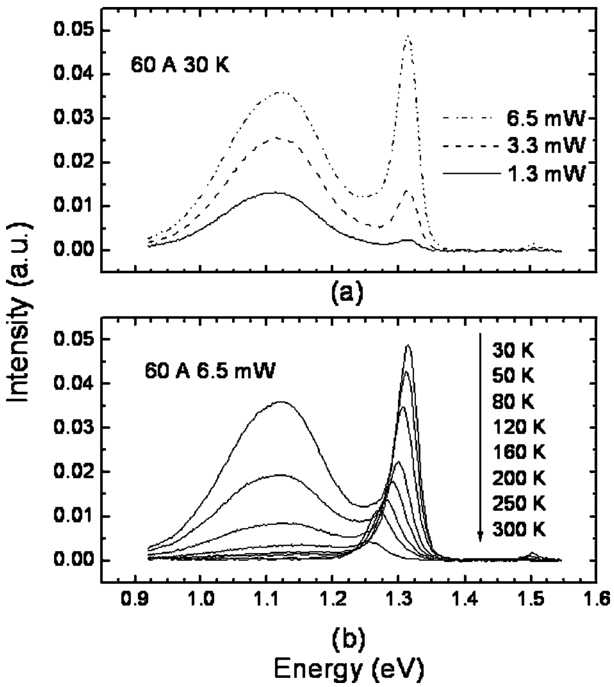

FIG. 2. (a) Power and (b) temperature dependences of the PL spectra of the 60 Å GaAsN sample with N=1.8%. At low excitation power, the 1.1 eV deep-level emission dominates the QW emission; however, at high excitation power, the QW emission dominates the deep-level emission.

B. Power and temperature dependence of the 1.1 eV emission

Figure 2 shows the power and temperature dependences of the PL spectra of the 60 Å GaAsN sample with N =1.8% to elucidate the recombination mechanism of the deep-level emission. At low excitation power (1.3 and 3.3 mW), the QW emission is weak and the spectrum is dominated by the deep-level emission, as shown in Fig. 2(a). As the excitation power increases, the deep-level emission gradually becomes saturated and, at 6.5 mW, is dominated by the QW emission. This finding indicates that the photogenerated carriers initially occupy the deep level because it is at a lower energy than the QW emission. When the power excitation is raised, further photogenerated carriers must occupy the higher QW state because the concentration of the deep level is limited. The line shape of the 1.1 eV emission is rather symmetrical as the QW emission, consistent with the fact that both emissions involve the same QW EGS. The temperature dependence in Fig. 2(b) shows that the intensities of both the QW and the 1.1 eV emissions decrease as temperature is increased. The QW peak displays a clear redshift with increasing temperature, whereas no shift in the 1.1 eV emission is evident because of linewidth broadening.

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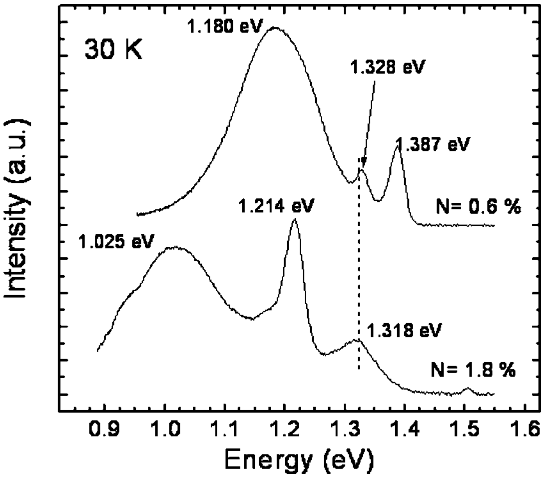

FIG. 3. 30 K PL spectra of the 250 Å GaAsN samples with N=0.6% and 1.8%. Besides the QW and the 1.1 eV emissions, each spectrum shows an additional peak at 1.328 (1.318) eV for N=0.6% (1.8%), which is attributed to a transition between the deep level and the GaAs CB.

The data are not sufficiently detailed to draw any conclusions on the thermal effect of wave-function localization of the deep level.

C. Composition dependence of the deep-level emissions

Figure 1 shows an additional weak peak at 1.318 eV in the 250 Å sample. This peak is not clearly seen in the other samples probably because of its proximity to the QW peak. Figure 3 shows the composition dependence of this peak in the 30 K PL spectra of the 250 Å GaAsN samples with N =0.6% and 1.8%, as indicated by the vertical dashed line. For a GaAsN thickness of 250 Å, the QW confinement effect is negligible and the QW emission energy can be regarded as the GaAsN band gap, regardless of whether the band lineup is type I or II. Increasing the N content shifts the QW emission from 1.387 to 1.214 eV and the deep-level emission from 1.180 to 1.025 eV. As discussed above, the energy separation between these two emissions is the deep level position above the GaAsN VB edge, which is 0.207 and 0.189 eV for N=0.6% and 1.8%, respectively, as shown in the schematic band diagrams in Fig. 4, in which the deep level is shown by a dashed line. For an assumed zero VB offset and a GaAs band gap of 1.505 eV, the defect level would be at 1.298 and 1.316 eV below the GaAs CB edge for N=0.6% and 1.8%, respectively. Notably, these levels are comparable to the additional weak emissions at 1.328 and 1.318 eV observed in Fig. 3 for N=0.6% and 1.8%, respectively. Therefore, these emissions are assigned to transitions between the GaAs CB edge and the deep level, and the differences of 0.03 and 0.002 eV are attributed to the VB offsets. This result shows that the band alignment is type II with a very small VB offset. Sakai *et al.*[5] theoretically predicted the type II alignment, and Kitatani *et al.*[8] used x-ray photoelectron spectroscopy (XPS) to support this prediction. Sun *et al.*[9] also reported a type II alignment with a VB offset of 0.04 eV for N=1.5%, which is close to the value of 0.028 eV that was obtained by XPS.[8] However, the very small VB offset (0.002 eV) for N=1.8% suggests the possibility of a transition to type I as the N content increases. This possibility may explain the type I alignment that was also predicted by first-principle calculations[10] and supported by PL[11] and hole-confinement measurements.[12] N content must be further increased to verify this claim.

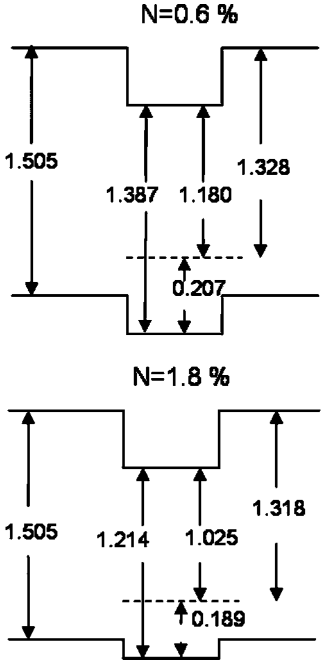

FIG. 4. Schematic energy band diagrams for 250 Å GaAsN samples with N=0.6% and 1.8%, respectively. The diagrams illustrate the deep levels and their experimentally observed transitions.

The energy perturbation of the deep level that is caused by the band discontinuity across the interface must also be considered. The strong localization of the wave function for a carrier trapped on a deep defect state[19] causes the energy perturbation of the deep level to be significant only within a few angstroms around the interface. In the GaAs/GaAsN system in which the VB offset is very small, a negligible energy perturbation of the deep level can be expected. Thus, the deep level is shown as continuous across the interface, as illustrated in Fig. 4. This result suggests the possibility of using this deep level as a common reference[13] for probing the interfacial band structure of a heterostructure.

D. Effect of annealing on deep-level emissions

As shown in Fig. 4, the CB offset increases from 0.148 to 0.293 eV as the N content increases from 0.6% to 1.8%, suggesting a downward shift of 0.145 eV in the GaAsN CB edge. This downward shift does not move the deep level downward. Instead, the deep level is shifted upward by 0.01 eV. If this small upward shift is neglected, then the deep level is tied to the GaAs band edge. This is a characteristic of a GaAs point defect rather than a N-related defect. This defect can be effectively removed by postgrowth annealing. Figure 5 shows the 30 K PL spectra of the 40 and 175 Å samples (N=1.8%) after annealing at 800 °C for 3 min. A comparison with the spectra of the as-grown samples in Fig. 1 reveals that annealing produces no signifi-

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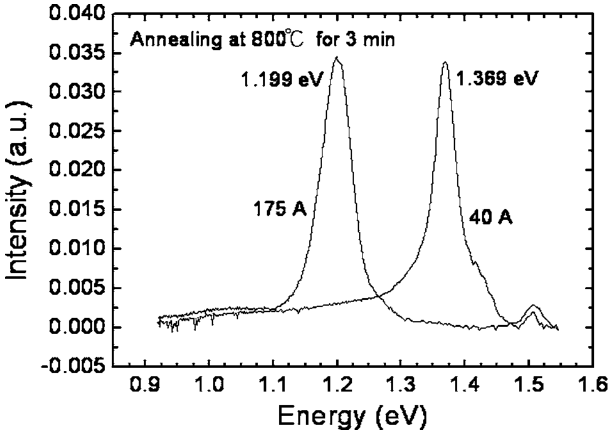

FIG. 5. Effect of annealing at 800 °C for 3 min on the 30 K PL spectra of the 40 and 175 Å GaAsN samples with N=1.8%. The deep-level emissions seen in Fig. 1 are nearly absent.

cant energy shift of the QW emission, suggesting no apparent interdiffusion. This is consistent with the secondary ion mass spectroscopy (SIMS) result that shows no significant drop of the N concentration in the QW region after annealing. In both samples, annealing increases the intensity of the QW emission. This improved efficiency can be attributed to the removal of deep levels. Notably, the 1.1 eV emission becomes nearly invisible after annealing, suggesting that annealing can remove the corresponding deep level. This finding is consistent with the assignment of a GaAs point defect for the 1.1 eV emission rather than N-related impurities.

Another reason to exclude N-related defects, such as N interstitials, for the 1.1 eV emission is that if they were involved, the intensity of the 1.1 eV emission would increase with the N content from 0.6% to 1.8%. However, the experimental data in Fig. 3 show no such trend. Thus, the deep level originates from a GaAs point defect. This level is at 0.177 (0.187) eV above the GaAs VB edge for N=0.6% (1.8%). In view of this energy position, we speculate that the deep level is associated with gallium vacancies V_{Ga} which were reported to be at ~0.2 eV above the GaAs VB edge and was a radiative defect.[20–22] The transition between this defect and GaAs CB would emit at ~1.25 eV which was commonly observed in liquid encapsulated Czochralski (LEC) GaAs substrates.[20] Chiang and Pearson[21] and Ohbu *et al.*[22] observed a similar emission at ~1.255 eV in GaAs films grown at low temperature and assigned it to V_{Ga}. This defect is very close to the 1.1 eV deep level. In view of the energy proximity, the deep level is assigned tentatively to V_{Ga}. This level may be the hole trap at 0.23 eV previously observed in p-type $\mathrm{In_{0.07}Ga_{0.93}As_{0.98}N_{0.02}}$ on GaAs by deep-level transient spectroscopy (DLTS).[23] The presence of V_{Ga} is supported by the previous observation of EL6 (As_i or As_i-V_{Ga} complex) and EL2 ($\mathrm{As_{Ga}}$) traps by DLTS in GaAsN/GaAs samples.[15,24] If As_i is available, the presence of V_{Ga} would favor the formation of $\mathrm{As_{Ga}}$ according to the reaction:[25] $\mathrm{As}_i + V_{\mathrm{Ga}} \rightarrow \mathrm{As_{Ga}}$. Low-temperature grown GaAs is known to contain a high concentration of point defects such as $\mathrm{As_{Ga}}$ and V_{Ga};[26] therefore, the presence of V_{Ga} in the GaAsN layer is reasonably suggested to be due to the low-temperature growth of the GaAsN layer to enhance the incorporation of N and suppress the compositional fluctuation. The results hereinto show that the V_{Ga}-related deep level is radiative and is tied to the GaAs band edge. Therefore, purposely introducing this level enables the GaAsN/GaAs band offset to be evaluated by analyzing its related transitions.

IV. CONCLUSIONS

Deep-level emissions of GaAsN/GaAs SQW structures were investigated. PL spectra show prominent emission at ~1.1 eV, which exhibits a similarly sized confinement effect as the QW emission. This emission is attributed to a transition between the QW electron ground state and a deep level. This deep level is tied to the GaAs band edge and, because of its energy position, is tentatively assigned to V_{Ga}. Furthermore, the PL spectra display an additional emission, which is attributed to a transition between the deep level and the GaAs conduction band. Using this deep level as a common reference, the GaAsN–GaAs band alignment is evaluated to be type II with valence-band offsets of 0.03 and 0.002 eV for N=0.6% and 1.8%, respectively.

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