Alloy disorder effects on the room temperature optical properties of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$quantum wells

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The effect of alloy disorder on the optical density of states and the average room temperature carrier statistics in Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ quantum wells is discussed. A red shift between the peak of the room temperature photoluminescence and the surface photovoltage spectra, that systematically increases with the nitrogen content within the quantum wells is observed. The relationship between this Stokes’ shift and the absorption linewidth in different samples suggests that the photoexcited carriers undergo a continuous transition – from being in quasi-thermal equilibrium with the lattice, to being completely trapped by the quantum dot-like potential fluctuations – as the nitrogen fraction in the alloy is increased. The values of the ‘electron temperature’ inferred from the photoluminescence spectra are found to be consistent with this interpretation.

Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ dilute nitride alloys[1, 2] provide an attractive possibility of designing quantum wells (QWs) which are optically active in the 1.3 µm range, provide strong carrier confinement and control of strain and band alignments, and can be grown on GaAs substrates. A number of experiments on this system indicate that the very reasons for the large downward bowing of the optical energy gap, namely the small size and the much larger electronegativity of the nitrogen atoms in comparison with the group-V host, are also the ones responsible for creating a distribution of localized states and compositional fluctuations in a diluted nitride sample. Such disordered QWs may behave like ensembles of quantum dots, capable of localizing charge carriers in the low energy tail arising out of spatially varying disorder strength. Signatures of this carrier localization appear, for example, in the anomalies in the temperature dependence of the photoluminescence(PL) peaks and linewidths. Many previous PL[2, 4, 5, 6], PL excitation[6], photoreflectance[2, 4, 7] and surface photovoltage(SP Vand surface photovoltage(SPV))[8] studies have reported such anomalous behavior, along with a systematic and significant degradation of the transition linewidths and luminescence efficiency with increasing nitrogen content in the samples and a Stokes-like shift[2, 3, 4, 5, 6] between the maxima of the optical density of states(inferred from PL excitation or photoreflectance) and the (typically low temperature) emission spectra.

In this letter, we have attempted to add to the earlier qualitative studies on electron localization with a more quantitative analysis within the framework of different theories of Stokes’ shift in disordered QWs[3, 10, 11, 12, 13, 14].

**Experimental.** All the samples were grown by low pressure metal-organic vapor phase epitaxy[15] on GaAs substrates. The structure consisted of a GaAs buffer layer on which a single 6 – 7nm thick Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ QW sandwiched within ~ 8nm GaAsN barrier layers was grown. This was capped by a 100nm thick GaAs layer.

![](image.png)

**FIG. 1:** SPV and PL spectra measured at room temperature in Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ QWs. See text for samples’ details.
of measurements were corrected for the system response. The thickness and composition of the QW and barrier for each of the samples was determined by matching the high resolution X-ray diffraction profile with that simulated using dynamical diffraction theory (Philips X’Pert Epitaxy 3.0). The values determined from the simulation were consistent with the estimates made from the growth parameters, as well as with calculated PL transition energies using the phenomenological model of Chow et al. 17.

The disorder effects on optical properties we have studied here are primarily determined by the changes in the nitrogen content of the quaternary QW 18. The small variations in nitrogen content (1.3 – 1.5%) and thickness(8 – 9nm) in the GaAsN barrier, as well as the variation in the QWs’ indium content (40-44 %, as inferred from the X-ray simulations) have little effect on the confinement energies and practically no effect on the linewidths of interband transitions 19. The samples in Fig.1 (a)-(e) have \( y = 0.009, 0.011, 0.013, 0.014 \) and \( 0.017 \) respectively with an approximate uncertainty of around \( \pm 0.001 \) and \( x = 0.42 \pm 0.02 \). SPV measurements were performed in ‘soft contact’ mode. A detailed discussion of the apparatus and the measurement technique has already appeared in reference 20.

Results and Discussion. Fig 2 shows the SPV and PL spectra measured on five different QW samples whose compositions were discussed earlier. It is evident that (1) the linewidth of the emission and sharpness of the SPV spectra degrade with a shift in the transition energies to lower values (increasing nitrogen content), and (2) the Stokes’-like shift also increases with the linewidth. Quantitative estimates of these observations are given in Fig.3 where this Stokes’ shift is plotted against the SPV FWHM. This Stokes’-like shift arises because an absorption measurement like SPV (essentially) reflects the optical density of states but the emission spectrum also necessarily has to involve the distribution of carriers occupying these states just before radiative recombination. A non-resonant PL experiment, like the one reported here, involves carrier excitation in the GaAs cap region. These carriers then migrate to the Ga1-xInxNAs1-y QW and may randomly diffuse into any of the local potential minima. If the strength of the energy barriers corresponding to the local minima trapping these carriers is larger than the thermal energy, carriers will not be able to thermalize within the finite recombination times. The PL spectra would then preferentially reflect the density of states \( \rho_0 \) corresponding to the local energy minima (‘minimum distribution’) 14, i.e., \( PL(E) \sim \rho_0(E) \). The absorption spectra, on the other hand, should not discriminate between the troughs and crests of the potential energy surface. This leads to a universal picture of Stokes’ shift, first proposed by Yang, Wilkinson, et al. 8, which is expected to be valid in the limit of very large disorder strength, low temperature or both. This theory predicts that the Stokes’ shift (SS) should be related to the absorption FWHM (\( \Delta \)), \( SS/\Delta = 0.553 \). On the other hand, in the high temperature limit where the fluctuations in the potential energy landscape are small compared to the lattice temperature and the carriers are in quasi-equilibrium with the lattice, one would expect the PL to be also affected by the thermal occupation factor, i.e., \( PL(E) \sim \rho_0(E) \exp(-E/k_BT_c) \). With the assumption of a Gaussian density of states, it trivially follows 14, 15 that \( SS=0.18\Delta^2/k_BT_c \) in this case. The predictions of the two theories are also plotted in Fig.2. We observe a crossover from the thermalization induced
almost similar lattice and electron temperatures, the effective 
Note that while the samples with least amount of nitrogen has 
function 
exp(−E/KBTC)

The same room temperature PL spectra as in Fig. 1, but now plotted on a semi-log scale (scatter plot). The straight lines (solid lines) depict curves corresponding to different to the equation log y = A − E/kBTc where kB is the Boltzmann constant, and Tc corresponds to an effective ‘electron temperature’ marked on each line and A is an arbitrary number. Note that while the samples with least amount of nitrogen has almost similar lattice and electron temperatures, the effective electron temperature increases as a function of nitrogen content within the QW (see text).

FIG. 3: The same room temperature PL spectra as in Fig. 1 but now plotted on a semi-log scale (scatter plot). The straight lines (solid lines) depict curves corresponding to different to the equation log y = A − E/kBTc where kB is the Boltzmann constant, and Tc corresponds to an effective ‘electron temperature’ marked on each line and A is an arbitrary number. Note that while the samples with least amount of nitrogen has almost similar lattice and electron temperatures, the effective electron temperature increases as a function of nitrogen content within the QW (see text).

Stokes’ shift to a disorder induced Stokes’ shift as the compositional disorder is increased in the samples, with the least and most disordered samples falling on the first and the second curves respectively.

To gain further insight into the carrier distribution, the room temperature PL plots are now depicted on a semilog scale in Fig. 3. The high energy tail of the spectrum is expected to reflect the carrier distribution and can therefore be fitted to the Boltzmann distribution function A exp(−E/kBTc), where kB is the Boltzmann constant, Tc is the ‘electron temperature’ [13] and A is an undetermined constant since the PL intensity is measured in arbitrary units. We observe that this carrier temperature gets larger with the increase of the nitrogen content in the samples. For the first sample, the carrier temperature is almost exactly equal to the lattice temperature, indicating almost complete thermalization, which was also the conclusion of Fig. 2 reached independent of this analysis.

A simple interpretation of the high carrier temperature in disordered samples follows from the observation that one can look for an interpolation between the low and high temperature regimes by combining the two previously discussed relations for the PL spectra to a single expression of the kind, PL(E) ∼ p0(E) exp(−βE/kBTc), with the parameter 0 ≤ β ≤ 1 continuously interpolating the carrier distribution between the two extremes. Introduction of this parameter β amounts [21] to defining an effective carrier temperature Tc' = T/β > Tlattice, which will be larger in more disordered samples. The difference between carrier and lattice temperature thus provides a convenient measure of the sample quality.

Conclusions. We have presented a systematic experimental study of alloying induced carrier localization at room temperature in Ga1−xInxN0.5As1−y QWs. By independent assessments of the (1) relationship between the Stokes’ shift and absorption linewidths, and (2) the carrier temperature inferred from the high energy tail of the room temperature PL spectra in different samples, we have been able to establish that there is a crossover from the regime of complete carrier thermalization to the complete localization regime as the alloying disorder is increased. These methods provide quantitative means for a comparative assessment of different Ga1−xInxN0.5As1−y samples.

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[19] Very approximately, since \( \partial(\text{Gap})/\partial(\text{Composition}) \) is the measure of the alloy disorder, using the standard anti-crossing formula (discussed in reference [17]) for \( \text{Ga}_1-x\text{In}_x\text{N}_y\text{As}_{1-y}, \) we estimate, \( \partial E_g(x,y)/\partial x = 0.1eV \ll \partial E_g(x,y)/\partial y = 8eV \) for \( x = 0.4 \) and \( y = 0.01. \) This implies that even a 0.5% variation in nitrogen has a much stronger effect than a 5% variation in the indium content.

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