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Carrier confinement and fabrication effects in GaInAs-InP quantum wires and dots

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Abstract: We report a fabrication and luminescence study of GaInAs-InP single quantum wells down to lateral dimensions of 15nm. The changes in the energy position of the spectrum of wires and dots is explored as a function of processing parameters. Blue energy shifts of up to 8meV observed are too small considering the lateral dimensions and therefore processing induced strain has to be invoked to understand the weaker confinement in these structures. Tests of wet etching and annealing are reported.

There have been several reports on quantum wires and dots fabricated in lattice-matched GaInAs-InP quantum wells^[1-9]. The most striking feature has been the wide spread of reported confinement energies which, for example, for 40nm wide wires spans the range from 0-11 meV.

The aim of this work was to fabricate the smallest possible wires and dots by electron - beam lithography and reactive ion etching and to inspect the luminescence of these nanostructures particularly before and after a given processing step to gain an insight into the contributions to the final blue energy shift.

Several samples were used in this work, however the results presented here are from one sample grown by MOCVD on a semi-insulating InP substrate. It consisted of a 200nm InP buffer layer, a 7nm GaInAs quantum well and a 12nm InP top barrier. The fabrication process employed a Leica-Cambridge EBPg HR5 Beamwriter working at 50KeV. The exposure used varied from 36 $\mu\text{C}/\text{cm}^2$ for the 15 nm diameter dots, through 700 $\mu\text{C}/\text{cm}^2$ for 25nm wide wires to 1960 $\mu\text{C}/\text{cm}^2$ for high resolution 25nm diameter dots. The bilayer resist used was 2.5% BDH and 2.5% Elvacite. Then a layer of $\text{SrF}_2/\text{AlF}_3$ approximately 25nm thick was evaporated and lifted-off. The samples were reactive ion etched in CH_4/H_2 in a gas flow rate of 1 to 2, an etch pressure 30 mTorr at a rate of 31nm/min. The luminescence measurements were recorded in a standard system, using the 488nm line of an Argon laser exciting both the InP and GaInAs layers, a Ge detector and sample temperatures between 4 and 300K. The luminescence of the control sample is shown in Fig.1. Variations across the sample size to be patterned were within 4meV in the energy position of the quantum well emission.

Fig.1 4K Luminescence from as-grown sample.

The emission from dots as a function of dot diameter is shown in Fig. 2. The magnitude of the blue shift for a given lateral size is smaller than expected from rough calculations of exciton confinement in a GaInAs-InP wire with infinite walls. It is clear from this figure that there are other mechanisms giving rise to energy shifts of the emission from the quantum dots. There are several possible candidates including alloy fluctuations, impurities and or defects introduced during the etching process, quantum well thickness variations and strain in the etched structures. Concerning the localization related possibilities we compared the integrated luminescence emission from wires of the same width as a function of wire length. It is known from our work in high quality GaAs-GaAlAs wires [10] that with a random distribution of impurities in the quantum well material, the normalized integrated intensity of wires of decreasing length increases since statistically there is a smaller probability of shorter wires having a non-radiative exciton trap. Fig. 3 shows the integrated emission intensity against wire length for GaInAs-InP 100nm wide wires. The trend shown is opposite to that in GaAs-GaAlAs wires suggesting that exciton diffusion hardly occurs and therefore the emission observed from wires and dots in our material comes from localized excitons. This was further demonstrated by both power and temperature dependence of the emission line from the control sample: The integrated emission intensity followed a linear dependence on power over four decades confirming the emission originated from the fundamental transition in the quantum well. The temperature dependence of the emission energy followed the band edge of GaInAs and was successfully fitted with the expression $E_0(T) = E_0(0) + \alpha T^2/(T+\beta)$, with $E_0(0) = 0.862$ eV, $\alpha = 2.7 \times 10^{-4}$ eV/K and $\beta = 127$ K the temperature coefficient α compares well with those of GaAs, InP and InAs. Moreover, the temperature dependence of the full width at half maximum (FWHM) of the control sample (quantum well) emission exhibited a reduction from 14.2 to 12.3 meV when the temperature was raised from 4 to approximately 20K and then it increased again to a maximum value of 25 meV at 100K remaining in the range of 21-25 meV up to room temperature. This is shown in Fig. 4 opposite. This indicates that the broadening mechanisms responsible for the FWHM are very complex. At least four mechanisms are important here: impurity broadening, alloy disorder broadening, thermal broadening and electron-phonon interaction. Further work is in progress to quantify these contributions.

The effect of processing in the wire and dots luminescence spectrum was also studied. The reactive ion etching processes is known to create defects at least on the surface of the etched

Fig.2 Energy shift of 5K emission from dots against dot diameter.

Fig.3 5K Integrated emission intensity from 100nm wide wires against wire length.

Fig.4 Temperature dependence of the FWHM of control sample emission.

Fig.5 Emission from wires before (top spectra) and after (bottom spectra) annealing. (a) 20 nm wires and (b) 50 nm wires.

structures. An annealing step was carried out in two wire arrays under the following conditions: temperature = 400 C, annealing time = 2 minutes, gaseous environment = 95% Ar + 5% H₂. The luminescence spectrum before and after annealing are shown in Figs. 5a and 5b for the 20 and 50 nm wide wire arrays, respectively. In the case of the narrower wires the emission intensity decreased dramatically after annealing and the centre of the emission was shifted to higher energies by about 6 meV. In the case of the 50 nm wide wires the emission became significantly narrower, dropping in intensity by a factor of two and also shifting to higher energies by 7 meV.

In an attempt to remove physically the 'damaged' surface layer several annealed arrays were wet etched in 4 ml HCl : 4 ml H₂O₂ : 4 ml CH₃COOH. Fig. 6 shown the emission of an array of 30 nm diameter dots and a control area (mesa) after annealing and wet etching. With respect to the control mesa the dot luminescence peak is broader and shifted to higher energies by almost 12 meV with somewhat stronger intensity.

In as-grown samples with the largest FWHM in the quantum well emission spectrum, the wire and dot luminescence showed a broad high energy band above the heavy-hole1- electron1 transition. This high energy emission subsequently disappeared after wet etching suggesting that contribution to this high energy emission may have its origin in surface states created during the fabrication and the associated band-bending and not in hot luminescence due to the intrinsic 'bottleneck' effect[11].

Bypassing the annealing step, a fresh piece of the sample was processed in the usual way to fabricate 20 nm diameter dots and immediately after reactive ion etching it was subjected to wet etching in the solution mentioned above. Spectra of the dot array and of the control mesa are shown in Fig. 7. Compared to the control mesa the emission from dots became weaker, broader, although it was not as broad as the emission from the dry etched-only samples, and appeared blue shifted by 4 meV.

Fig.6 Emission from a control mesa (a) and 30 nm dots (b) after dry etching, annealing and wet etching.

Fig.7 Emission from a control mesa (a) and 20 nm dots (b) after dry etching and wet etching.

Conclusions

This study strongly suggests that the origin of the energy blue shift in GaInAs wires and dots results from a combination of factors which may include: strain, extrinsic centres, exciton confinement, etc and highlights the need to determine the role of these mechanisms and a way to control them.

Concerning further processing induced effects, annealing and wet etching and wet etching without annealing of the samples produced different emission peak energies at higher energies than the 2D control sample. The integrated intensity also varied in wires and dots by up to a factor of 10. The energy shifts arising from processing steps are similar to those measured as a function of decreasing lateral size.

There is a clear need to model these structures considering the factors mentioned above and quantify them in order to understand the nature of the actual confinement. The very small sizes achieved suggest that these observations may also be relevant to directly-grown wires and dots

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