Time-resolved photoluminescence microscopy of GaInAs/GaInAsP quantum wells intermixed using a pulsed laser technique

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High spatial resolution time-resolved photoluminescence has been used to study GaInAs/GaInAsP quantum-well structures selectively intermixed using the pulsed photoabsorption-induced disordering technique. Photoluminescence decay measurements at wavelengths >1.3 μm were obtained using novel high-efficiency photon-counting detectors and were found to correlate spatially with the observed luminescence blue shift in these structures. Results indicate a reduction in the nonradiative recombination time of nearly two orders of magnitude as a result of this intermixing technique. © *1996 American Institute of Physics.* [S0021-8979(96)06312-8]

In recent years the selective intermixing of III–V quantum-well (QW) structures has been achieved by techniques including impurity-induced disordering, impurity-free vacancy disordering and laser-induced disordering.[1] A technique particularly suited to the GaInAs/GaInAsP quantum-well system is photoabsorption-induced disordering (PAID), which uses the differential absorption of incident cw radiation within the structure to cause intermixing.[2] The lateral spatial selectivity of the technique is determined by short-range thermal diffusion from the absorbing regions. Spatially-resolved steady-state photoluminescence (PL) spectroscopy measurements of selectively intermixed samples indicate a lateral interface abruptness of ~ 100 μm.[3]

More recently, the use of high-power pulsed lasers for sample disordering by localized transient heating within the crystal has been reported.[4] Disruption of the lattice due to rapid thermal expansion is thought to lead to an increase in the point defect density. These point defects subsequently diffuse during the high-temperature annealing stage, and enhance the QW intermixing. In order to minimize the effects of lateral diffusion, laser pulses were used of a similar duration to the calculated thermal time constant in InP. In the earlier work[4] blue shifts in the PL wavelength of up to 180 nm were observed at a wavelength of 1.55 μm. Masking of the sample during irradiation gave a lateral spatial resolution of $\leqslant 25$ μm for the technique.

In this article we report room-temperature time-resolved photoluminescence (TRPL) measurements on the samples described in Ref. 4. These measurements were made using a microscope-based instrument, derived from an Edinburgh Instruments LifeMap and described in detail elsewhere.[5] The excitation source used in these measurements was a passively *Q*-switched laser diode[6] which emitted 10 ps duration pulses of energy ~ 4 pJ at a wavelength of 860 nm. TRPL measurements were made in the spectral region 1.32–1.46 μm, with wavelength discrimination provided by optical bandpass filters. A schematic representation of the TRPL instrument is shown in Fig. 1. The laser excitation is directed onto the sample and the PL routed to the detector by polarization optics inserted in the microscope column.

The TRPL measurements were made using the time-correlated single-photon counting technique (TCSPC).[7] As shown in Fig. 1, a fraction of the laser output is detected by a silicon avalanche photodiode operated in the analog mode and this provides the start signal for a time-to-amplitude converter (TAC). The TAC produces an output pulse with an amplitude proportional to the time interval between the start and stop inputs. This is then digitized by an analog-to-digital converter (ADC) and stored in a multichannel analyzer (MCA).

The photon-counting detector was a commercially available small area (~ 30 μm diameter) germanium avalanche photodiode (GPD, GAV30) cooled to 77 K and biased 0.6 V above breakdown to enable a single photon to generate a large avalanche response. These Ge detectors have only recently been exploited for TRPL measurements utilizing their high-quantum efficiency in the photon-counting mode.[8] With this instrument, PL emission from similar samples has been measured at photogenerated carrier densities as low as $\sim 10^{15}$ cm^{-3}, exhibiting excellent sensitivity when compared to alternative time-resolving techniques such as nonlinear pump–probe[9] or upconversion luminescence[10] measurements. The Ge single-photon avalanche diode (SPAD) is operated in a gated active quenching circuit (AQC).[11] TRPL measurements at wavelengths up to ~ 1.5 μm are achievable with this system,[8] with an instrumental temporal half-width of ~ 300 ps.

The samples under investigation were nominally undoped, expitaxial waveguide structures, grown by metal-organic vapor-phase epitaxy (MOVPE) on an InP substrate. The multiple QW (MQW) structure consisted of five periods of 85 Å GaInAs wells with 120 Å GaInAsP barriers bounded by two graded index (GRIN) GaInAsP confinement layers with a capping layer of InP. Disordering was carried out by irradiation with ~ 7 ns duration pulses at a wavelength of 1064 nm from a *Q*-switched Nd:YAG laser. The pulse rep-

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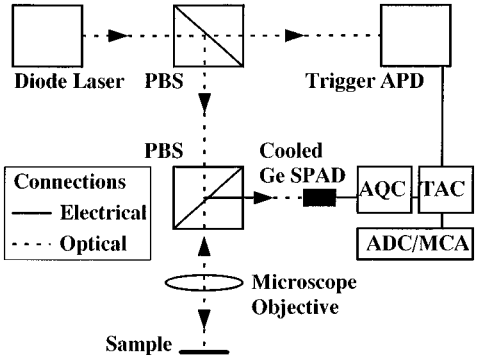

FIG. 1. A schematic representation of the TRPL setup showing the optical routing of the laser excitation and PL by polarizing beam splitters (PBSs). The components of the TCSPC electronics are indicated: trigger APD; AQC; TAC; ADC; and MCA. The Ge-SPAD is biased above breakdown for ~200 ns per 1 ms laser cycle by a square-wave voltage input to the AQC (not shown).

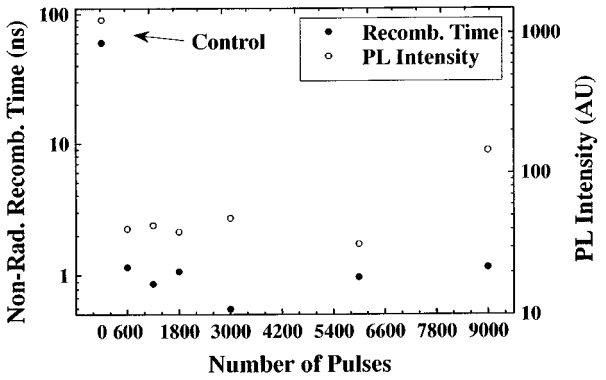

FIG. 3. The effect on the nonradiative recombination time and the PL intensity of number of PAID pulses from a Nd:YAG laser. All samples, including the control, have been annealed.

etition frequency was 10 Hz and the energy density incident on the samples was 5 mJ mm^{-2}. This irradiation was followed by thermal annealing at 700 °C. Analysis of steady-state PL measurements indicated that there were similar levels of intermixing in each of the five quantum wells in this sample.

The six samples had received between 600 and 9000 pulses and had then been annealed for 360 s along with the unirradiated control sample. TRPL measurements were made at room temperature on all seven samples. Figure 2 shows three PL decays: two from the control sample (not exposed to laser treatment) and one from a sample treated with 1800 pulses. The slowest decay in the figure (time constant ~60 ns) was obtained from the control sample using a 30-μm-diam excitation spot while the intermediate decay (time constant ~4.6 ns) was obtained with a much smaller, ~1.5 μm, excitation spot. The combination of imaging optics and small area detector meant that a detection area of only ~4 μm diameter was sampled at the center of the excitation spot. The PL measurements over such small excitation areas can be significantly affected by lateral carrier diffusion out of the detection area; however, the combination of large excitation areas and relatively small detection areas will serve to negate the effects of lateral carrier diffusion since carriers will diffuse both into and out of the detection areas at equal rates. There may be some increase in Auger and radiative recombination at the high carrier densities resulting from focusing the excitation pulse. The excited carrier density was $\sim 6\times10^{10}$ cm^{-2} for the 30-μm-diam excitation spot and $\sim 3\times10^{12}$ cm^{-2} (over the 4-μm-diam detection region) for 1.5-μm-diam excitation.

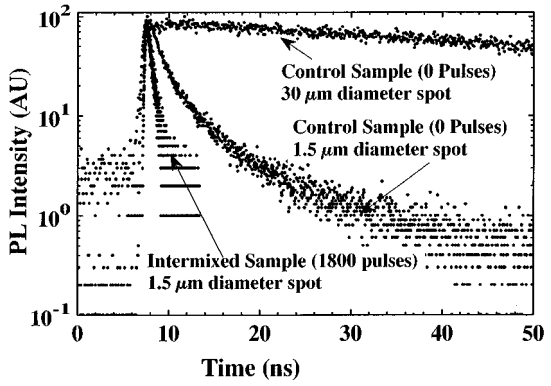

FIG. 2. PL decays, shown on a semilogarithmic plot, from the control sample and a sample intermixed by 1800 laser pulses. The decays resulting from excitation with a 1.5-μm-diam spot have decay constants (measured as the weighted average of a two-exponential fit) of ~4.6 and ~0.4 ns for the control and treated samples, respectively. The longest decay shown, from the control sample, was measured using a 30 μm excitation spot diameter to eliminate diffusion resulting in an exponential decay with time constant ~60 ns.

Significantly, the PL decay from the PAID processed sample in Fig. 2, measured using the small excitation spot, shows a reduced PL intensity and a further factor of 10 increase in decay rate (time constant ~0.4 ns). Since the decay rate from the PAID processed sample changes little with increasing spot size, a dramatic reduction in the carrier recombination time due to the dominance of nonradiative defect-mediated processes is implied.[12–14]

Carrier recombination in QWs is expected to be dominated by linear nonradiative recombination at the well–barrier interfaces.[13] The carrier dynamics were modeled using the 2D diffusion equation. The model assumed that the excitation had a Gaussian spatial profile of known dimension and reconvolution analysis was used to fit the PL data using a linear recombination time τ and ambipolar diffusion coefficient D as free parameters.[15] The PL decay measured using large area excitation showed a nonradiative PL decay of ~60 ns. Using this value in the diffusion model gave a best-fit value of ~1.8 $cm^2\ s^{-1}$ for the diffusion coefficient D. These results are comparable with values of τ and D measured using other techniques in unprocessed InGaAs-based III–V QWs.[9,16] By contrast, the sample which had been intermixed with 1800 pulses gave best-fit values of $\tau \sim 1$ ns and $D \sim 2$ $cm^2\ s^{-1}$.

Figure 3 shows the results obtained from the full series of TRPL measurements on the seven annealed samples. All of the measurements shown in Fig. 3 were obtained using a 1.5-μm-diam excitation spot and the nonradiative recombi-

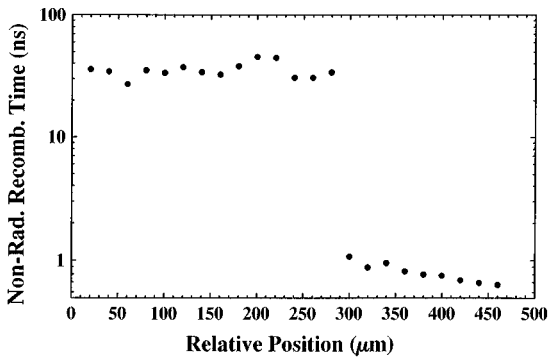

FIG. 4. Nonradiative recombination time as a function of lateral position across the sample, half of which has been irradiated. The excitation spot diameter was 20 μm. The boundary may be seen with a precision of better than 20 μm.

nation times plotted are best-fit values from the linear recombination and diffusion model discussed above. From Fig. 3 it is apparent that the effect of as few as 600 pulses is to markedly reduce the linear carrier recombination time from ~60 to ~1 ns. This reduction in recombination time, observed together with a corresponding reduction in PL intensity, is consistent with an increase in the nonradiative recombination rate. On further increasing the number of pulses beyond 600, both the recombination time and PL intensity show little further change. This compares well with the results obtained from the steady state PL measurements on these samples[4] which show an initial abrupt shift in the peak emission wavelength as the degree of optically induced disordering is increased.

The second experiment was to investigate further the spatial resolution of the pulsed QW intermixing technique. A sample was prepared with a metal mask suspended a few hundred μm above the surface during irradiation. The sample was treated with 12 000 pulses and annealed for 180 s at 700 °C. The PL peak at 77 K was blue shifted from ~1.46 to ~1.36 μm, from the masked to exposed side, as described previously.[4] TRPL measurements were made using a 20-μm-diam excitation spot, moving the sample by increments of 20 μm between measurements—the precision being limited by the mechanical precision of the translation stage used. The nonradiative recombination time was obtained by fitting the data to the same diffusion model described above and is plotted in Fig. 4 as a function of position.

The results indicate that the interface is clearly defined with a precision of better than 20 μm as the recombination time reduces from 35 ± 5 ns in the masked region to <1 ns in the exposed region. It is noticeable that the nonradiative decay times measured for the control sample and that measured for the masked side of the sample shown in Fig. 4 are different. This difference is thought to be in part caused by the relatively low statistical accuracy of the measured PL data at long times after the start of the decay. In addition there may be slight variations in material quality between the two samples.

Further work will concentrate on masking the sample using absorbing thin films deposited directly on to the epitaxial structure. Consequently, the TRPL measurements can be attempted at high spatial resolution, which will ultimately be limited to ~1 μm by diffraction at the microscope objective.

In conclusion, TRPL measurements of intermixed GaInAs/GaInAsP QW material using sensitive photon-counting detection have been demonstrated. These measurements have shown that the nonradiative recombination time in GaInAs/GaInAsP quantum wells can be reduced by two orders of magnitude following treatment with pulsed PAID, and that there exists lateral spatial correlation of the PL decay time and the PL blueshift. This work has demonstrated the practical value of novel Ge photon counting detectors in a high spatial resolution microscope system. The quantitative measurements of nonradiative recombination time and ambipolar diffusion coefficient provide valuable information which will allow greater flexibility in engineering both the band-gap and recombination time in future integrated optoelectronic devices fabricated using this, or similar, intermixing techniques in this material system.

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