Interdiffused quantum-well infrared photodetectors for color sensitive arrays

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(Received 4 March 1999; accepted for publication 23 June 1999)

Proton implantation and rapid thermal annealing were used to tune the infrared spectral response of quantum-well infrared photodetectors (QWIP) by up to 1.4 μ m. Multiple proton implants at energies between 200 and 420 keV were used to create homogeneous quantum-well intermixing throughout the device's multiple-quantum-well structure. Photoluminescence and spectral response measurements were used to study the effect of proton implantation on QWIPs for a series of doses up to 3.5×10^{15} protons cm⁻². By using a mask during implantation, a method of constructing a color sensitive array is proposed. © *1999 American Institute of Physics*. [S0003-6951(99)02333-5]

Quantum-well infrared photodetectors (QWIPs) have been the focus of much attention for use as large area thermal imaging arrays.¹ A QWIP array that could measure the intensity at two or more different infrared wavelengths would improve the ability of these devices to determine the temperature of objects. Two-color QWIPs have been proposed by several groups.^{2–4}

Chiang *et al.*⁵ demonstrated a two-color QWIP made by growing two stacks of quantum wells on top of each other. The parameters in each of the two stacks were designed to detect infrared (IR) radiation at different wavelengths. An n^+ GaAs contact layer was grown between the two detectors so that they could be contacted separately. However, making an electrical connection to this center layer is difficult even with a single detector, and may limit the use of this technique with large arrays.

Voltage tunable QWIPs have also been developed.^{6–8} Chiang *et al.*⁷ tuned IR spectral response by varying the QWIP's operating bias. They attribute the tuning to the quantum confined Stark effect which redistributes quantum-well energy levels.⁷ Bandara *et al.*⁸ used a multiple quantum-well structure with groups of three quantum wells of different widths. The photoconductive gain from each of the quantum-well's widths was sensitive to the applied bias, and since each of the well widths corresponded to different spectral responses, a voltage tunable QWIP was realized.

In this letter, we propose a new method for producing two- (or even multi-) color QWIP arrays by selectively tuning the spectral response of the individual mesas. The method combines two adjacent mesas with different spectral response to form a single pixel of the IR image. Interfacing this QWIP array is compatible with conventional silicon ("flip chip") readout circuit technology. The rest of this letter outlines and demonstrates a practical way to create such a device.

Quantum-well intermixing (QWI) is a post-growth technique which alters a quantum-well's energy bandgap profile.^{9,10} A typical quantum well has a rectangular energy bandgap profile in the growth direction. Interdiffusion of the barrier and well materials (i.e., Al from the AlGaAs barriers and Ga from the GaAs wells) leads to changes in the shape of the rectangular well into a smooth function approximated by two error functions.¹¹ This has the effect of altering the energy eigenstates in the well, which affects the intersubband energy regime.

Steele *et al.*¹² have used thermal annealing to alter the spectral response of QWIPs. However, this method of QWIP intermixing could not be used to make two-color QWIP array, since it causes intermixing across the whole wafer, rather than in a specific mesa. Even the rather weak effects of laser induced thermal intermixing¹³ would be unlikely to achieve sufficient resolution due to the good thermal conductivity of GaAs based alloys.

We believe that ion implantation induced intermixing offers the best method of tuning the IR spectral response of a QWIP with high spatial precision. The high spatial resolution is achieved by placing a mask on top of the QWIP wafer during irradiation. Tan *et al.*⁹ have shown that proton implantation produces large shifts in photoluminescence (PL) of single quantum wells, with better recovery of PL signal compared with the use of heavier ions such as As. Therefore, proton implantation induced intermixing was chosen for our study. This letter is the first systematic study of ion induced QWI using multiple energy protons in QWIPs.

Recently, Sengupta *et al.*¹⁴ have produced a detailed study of QWI in QWIPs using impurity free disordering. It is possible that this technique could also be used to selectively

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alter the spectral response of individual QWIP mesa.

The two QWIP wafers used in our study were grown by molecular beam epitaxy (MBE). They were designed to be bound-to-continuum¹ (BC) *n*-type QWIPs. Each wafer consisted of 50 sets of Si-doped ($\approx 10^{18}$ cm⁻³) 4.6 nm GaAs wells with 50 nm undoped Al_{0.3}Ga_{0.7}As barriers. The multiple-quantum-well structure was sandwiched between two 1 μ m n^+ GaAs contact layers.

QWI was achieved using a series of proton implants at different energies from 200 to 420 keV. Multiple energy implants were used to induce homogeneous QWI throughout the 50 quantum-well active regions of the QWIPs. Samples were implanted at room temperature with an aluminum mask placed onto the surface of the wafer so that only a specified region was implanted. After the multiple implantations the whole wafer was annealed under Ar flow at 950 °C for 30 s. Samples were loaded face down onto a piece of fresh GaAs during the annealing process to limit the loss of As from the surface. Finally, the wafers were processed into 250 $\times 250 \,\mu$ m² test devices using standard photolithography and wet etching. Au–Ni–Ge ohmic contacts were made on the top of the mesas. A 6 μ m period grating was etched to allow normal incidence operation.

IR spectral response data were acquired using a Fourier transform spectrometer. A bias of 2 V (field: 7.4 kV/cm) was applied across each device. PL spectra were obtained using a 0.5 mW green HeNe laser (543.5 nm) for excitation and the signal was detected by a charge coupled device (CCD) camera after dispersion by a 0.27 m spectrometer. The QWIP's n^+ GaAs top contacts were removed by wet etching prior to the PL measurements. PL spectra were obtained from each individual mesa. The sample temperature was maintained at 77 K.

Figure 1(a) shows the IR spectral response of a QWIP mesa implanted with a dose of 1.5×10^{15} protons cm⁻² and a nearby unimplanted mesa. The device parameters obtained from this sample are summarized in Table I. The implantation has caused the QWIP's peak wavelength to shift from 8.85 to 9.9 μ m. A reduction in responsivity (and PL intensity) was observed with increasing proton dose. Furthermore, current noise increased significantly for devices implanted with doses $> 2.5 \times 10^{15}$ protons cm⁻² making the detectivity of these devices impractically low (for example, a detectivity of 5.6×10^7 cm $\sqrt{\text{Hz}/\text{W}}$ was observed for a 2.5 $\times 10^{15}$ protons cm⁻² implanted mesa). These results suggest that further process optimization is necessary.

The success of the multiple implant QWI method is seen in the PL spectra [Fig. 1(b)]. The full width half maximum (FWHM) of the PL only increases marginally, which shows that the multiple energy implantation produced homogeneous intermixing throughout the 50 quantum wells. These results are favorable compared with the broadening in PL





FIG. 1. (a) IR spectral response and (b) photoluminescence spectra measured at 77 K. The dashed lines represent data from the mesa which was implanted with protons to a dose 1.5×10^{15} protons cm⁻² and the solid line represents data from the unimplanted mesa. Both regions were annealed at 950°C for 30 s.

and spectral response FWHM seen from impurity free disordering QWI.¹⁴

A systematic study of all our samples' IR spectral response as a function of proton dose is shown in the inset of Fig. 2. Note that the three different samples produced a consistent increase in response wavelength with proton dose, despite slight differences in their structures (seen by the differences in the unimplanted controls). Hence, controlled tunability of QWIP spectral response was obtained by varying the proton dose.

PL spectra give the energy between the lowest states in the conduction and valence bands. In previous studies of ion-implanted single quantum wells,⁹ PL was used to characterize the effects of QWI. PL was blueshifted as a result of QWI, which implies that the lowest energy level of the well rises.

Figure 2 shows the QWI induced energy shift in IR spectral response, (ΔE_{IR}), versus the shift in PL, (ΔE_{PL}). In a BC QWIP, the photocurrent is generated as a result of transitions between the lowest conduction band state and barrier (continuum) states. Therefore, a rise in the lowest conduction band state corresponds to a blueshift in PL (ΔE_{PL}) and a corresponding redshift in infrared spectral response (ΔE_{IR}). If intermixing affected both the conduction band and valance

TABLE I. Summary of results for a QWIP implanted with protons to a dose of 1.5×10^{15} protons cm⁻². The column entitled "IR Peak" refers to the peak wavelength of the QWIP's spectral response.

	PL peak nm (eV)	IR peak μm (meV)	Responsivity kV/W	Detectivity $\times 10^9$ cm/Hz/W
Unimplanted mesa	762.5 (1.626)	8.85 (140)	11	1.6
Implanted mesa	759.9 (1.632)	9.90 (125)	4	0.1



FIG. 2. Energy shift in the IR spectral response (ΔE_{IR}) plotted against energy shift in the PL (ΔE_{PL}). The shift in all instances is taken with respect to the unimplanted mesa. INSET: Dependence of peak spectral response wavelength on proton implantation dose. The points marked by the square and diamond correspond to QWIPs (separately) processed from different parts of the wafer. The circles correspond to QWIPs grown on a different wafer. The lines are drawn as guide to the eye.

band equally, then one would expect that $\Delta E_{IR} \approx \frac{2}{3} \Delta E_{PL}$ (assuming conduction band offset ratio is $\frac{2}{3}$). This $\frac{2}{3}$ ratio does not agree with our results; ΔE_{IR} is significantly greater than $\frac{2}{3}\Delta E_{PL}$ for samples with PL shifts between 7 and 18 meV. We explain this by the introduction of a second eigenstate in the conduction band well, which is consistent with QWI widening of the top of the well. That is, the QWIP changes from being of BC-type to a bound-to-bound¹ (BB)-type QWIP. Further evidence for this change is seen in Fig. 1(a). The reduction in IR spectral response FWHM from 2.1 to 1.9 μ m after implantation, indicates increase in confinement of the quantum-wells second bound state.

Calculations of Lee and Li¹¹ predict the introduction of the second eigenstate as a result of QWI. They have studied the theory of quantum-well intermixing for a BC QWIP with similar parameters to our devices. They model the well profile with error functions which are dependent on diffusion length, and solve Schrödinger's equation for the energy states using a finite difference method. They predict that the transition from BC to BB occurs with an intermixing diffusion length of 1.0 nm, which corresponds to an ion dose of 1.5×10^{15} protons cm⁻² for our samples.

Figure 2 gives insight into the effect of intermixing on QWIPs, it was obtained by determining the energy shift between each implanted mesa and its un-implanted control for IR spectral response (inset) and PL.

Lee and Li¹¹ also calculate that the responsivity should increase after the transition for BC to BB, due to the increased oscillator strength shown in Fig. 2. This is in contrast to a 64% drop in responsivity for the 1.5×10^{15} protons cm⁻² intermixed mesa. A diffusion of dopants from the well into barrier regions and the increase in nonradiative centers may be responsible for this discrepancy.

We have used the sample containing the 1.5×10^{15} protons cm⁻² mesa and its adjacent unimplanted mesa [see Fig. 1(a)] as a temperature sensor. The photocurrent signal of the implanted mesa was divided by the photocurrent signal of the unimplanted mesa with both mesas under 2 V bias. This ratio allowed blackbody radiation between 300 and 400 K to be measured with a resolution better than 5 K. We propose that a more sensitive temperature sensor could be constructed using a BB QWIP, since the spectral response FWHM of a typical BB QWIP is much narrower than a typical BC QWIP (such as the devices presented in this study).¹

In summary, we have used protons to implant specific areas of standard QWIP samples. After thermal annealing, the regions which were implanted showed significant intermixing with respect to the masked regions. Therefore, a twocolor QWIP was demonstrated. The ability to pattern a wafer using an implantation mask allows alternate mesas of large arrays to have alternating spectral responses. This concept shows promise as a way of making two- (or multi-) color QWIP arrays without altering the current technique of interfacing QWIPs with existing silicon readout chips.

This work was supported by the Australian Research Council and Australian Agency for International Development through IDP Education Australia under the Australia-China Institutional Links Program.

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