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Multiple quantum well optical waveguides with large absorption edge blue shift produced by boron and fluorine impurity-induced disordering

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Impurity-induced disordering of GaAs/AlGaAs multiple quantum well waveguide structures has been carried out using the neutral impurities boron and fluorine, introduced by ion implantation and followed by thermal annealing. Substantial blue shifts (up to 100 meV) in the absorption edge have been obtained and, for similar conditions, fluorine-induced disordering produces larger shifts than boron-induced disordering. Optical transmission measurements performed in slab and rib waveguides indicate that the additional contribution to the absorption coefficient associated with boron disordering is 15 dB cm^{-1} and with fluorine disordering is only 6 dB cm^{-1}.

Impurity-induced disordering (IID) has become established[1] as a technique for increasing the local band gap and reducing the local refractive index of quantum well layers. The refractive index changes can be used in a number of integrated optics applications, for example, to provide lateral optical waveguide confinement[2] or to form grating couplers.[3] However, the increase in band gap is potentially of greater significance since the nondisordered regions of a sample waveguide can be used as light sources or electroabsorption modulators while the disordered regions will not exhibit band-edge absorption and so can be used as low-loss optical windows or waveguides in integrated optoelectronic circuits (OEICs).[4,5] A major problem with the impurities commonly used in IID (mainly Si and Zn) is that they are ionized at room temperature and the resulting free carriers inevitably give rise to optical absorption, although Si (being a donor) is better than Zn in this respect. Since the impurity densities required for IID are typically greater than 10^{18} cm^{-3}, the absorption coefficient cannot be reduced much below 40 dB cm^{-1}, and indeed using Si IID propagation losses of $\simeq 71$ dB cm^{-1} (17 cm^{-1}) have been reported.[5] The lowest waveguide loss at the lasing wavelength of nondisordered material to appear in the literature[6] is 39 dB cm^{-1} (9 cm^{-1}), again obtained using Si IID; however, in this case only around 17 dB cm^{-1} of the total propagation loss was ascribed to free-carrier absorption because the Si appeared either to be compensated or not to be fully activated.

In this letter we report results for neutral impurity IID in multiple quantum well (MQW) layers, where the particular impurities investigated were boron and fluorine introduced using ion implantation.[7] Band-gap increases of up to 100 meV were observed, while, because the impurities are neutral dopants, waveguides formed in the disordered MQW exhibited only small increases in the near-band-gap absorption coefficient ($\simeq 6$ dB cm^{-1}). These results imply that IID is a practical technique for forming interconnecting waveguides in OEICs.

The MQW waveguide structure was grown as follows: a 0.5-μm-thick GaAs buffer layer was followed by 2.5 μm of $Al_{0.2}Ga_{0.8}As$, and finally by 44 periods of 80 Å of GaAs and 80 Å of $Al_{0.26}Ga_{0.74}As$, with all layers undoped. To simplify both the implantation requirements and the analysis by photoluminescence spectroscopy (PL), the MQW waveguide high-index region was grown at the top of the structure. The choice of the detailed parameters of the structure was intended to ensure that only the lowest order depth mode would propagate in the waveguide experiments.

The structure was grown by atmospheric pressure metalorganic vapor phase epitaxy (MOVPE) using the conventional reagents trimethylgallium (TMG), trimethylaluminum (TMA), and AsH_3 on a slice of undoped GaAs. Details of the equipment have been published previously.[8] In order to achieve high quality AlGaAs layers, the AsH_3 gas (20% in H_2) was processed at "point of use" by a eutectic melt of AlGaIn to remove oxygen and water, and both the TMG and TMA were adduct purified by the manufacturer (Epichem) to remove Si, Zn, and alkoxide impurities. The AlGaAs lower cladding layer was grown at 722 °C and the MQW structure was grown at 654 °C, since we have observed that MQW structures grown at this lower temperature exhibit lower background doping. During the cooling stage the slice was stabilized under flowing AsH_3. An electrochemical profile indicated that the MQW structure was fully depleted at zero applied voltage and that the residual doping of the AlGaAs cladding layer was 4×10^{15} cm^{-3} n type.

Samples typically of area about 1 cm^2 were implanted with either boron or fluorine ions with aggregate doses of 10^{14}, 3×10^{14}, 10^{15}, and 3×10^{15} cm^{-2}. In the case of boron, an approximately uniform dose throughout a depth of 0.7

μm was obtained by successive implants of 75% of the total dose at an energy of 200 keV and the remaining 25% of the dose at an energy of 100 keV. Because of operational difficulties only a single fluorine implant was used, at an energy of 300 keV, to give a range of 410 nm and a straggle of 161 nm.

Annealing was carried out in a conventional diffusion furnace with a high-purity flowing nitrogen atmosphere. The samples were mounted inside an enclosed high-purity graphite box so that the sample top surfaces were uppermost and exposed to a high local vapor pressure of arsenic provided from a small volume of gallium loaded with GaAs. All samples were capped with a plasma-deposited layer of 100–150 nm of either silicon dioxide or silicon nitride. It was found that the two types of capping layer gave very similar results and so SiO_2 capping layers were the main ones used because of the relative ease with which they could be removed if required. It was also concluded that, under our deposition and annealing conditions, any contribution to intermixing from vacancies created by diffusion of gallium into the SiO_2 capping layer[9] was relatively small.

Annealing was investigated over the range of temperatures from 750 to 890 °C (measured with a thermocouple embedded in the graphite box). Unimplanted, but capped, control samples were placed alongside the implanted samples to allow both the relative and absolute shifts of sample properties caused by the implanted impurities to be determined.

The annealed samples were investigated using PL at 18 K: spectra from an annealed control sample and samples implanted with fluorine and boron doses of 10^{14} cm^{-2} are shown in Fig. 1. The annealing times were 1.5 h for the control and for the F implant, and 2 h for the B implant, all carried out at 890 °C. Peaks were identified as follows: those labeled (a) are due to transitions in the AlGaAs layers, peaks (b) come from the (partially disordered) MQW structure, and peaks (c) come from the GaAs buffer layer and are due to band-to-band recombination at 819 nm and transitions via carbon acceptor levels at a wavelength of 830 nm. The small peaks (d) have not been definitely identified but are present at similar intensities in all the samples including the unimplanted starting material; however, at higher implant doses (10^{15} cm^{-2} range) or for longer anneals at lower temperatures these peaks become broader and more intense.

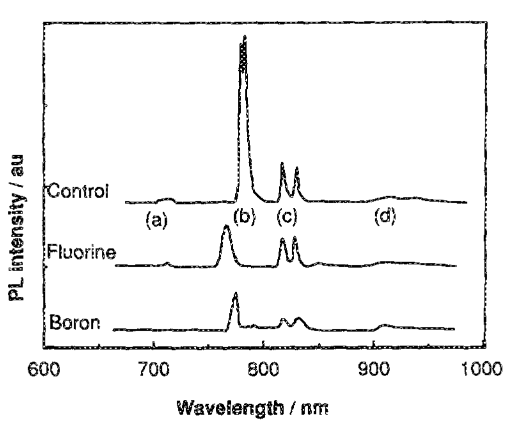

FIG. 1. Photoluminescence spectra at 18 K for starting material, a fluorine-disordered sample, and a boron-disordered sample.

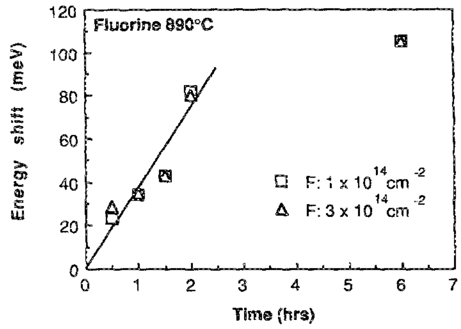

FIG. 2. Energy shift of the main PL peak of fluorine-disordered samples at implantation doses of 1 and 3×10^{14} cm^{-2}, as a function of annealing time. The points at 6 h for fluorine represent almost complete intermixing of wells and barriers.

Figure 2 shows the variation of the energy shift of peak (b) with annealing time at 890 °C for two different fluorine and boron implantation doses. Using fluorine the energy shift, at times for which the mixing process does not approach saturation, is over twice that observed using boron, results consistent with those previously reported by Hirayama *et al.*[7] which describe the intermixing of AlAs/GaAs superlattices grown by molecular beam epitaxy.

Room-temperature absorption measurements have been carried out on both slab and rib waveguides. Figure 3 shows endfire-coupled slab waveguide transmission measurements as a function of wavelength obtained using a Styryl-9M dye laser, for samples implanted with fluorine and boron doses of 10^{14} cm^{-2}. The plotted data include adjustments for the variation of the laser power with wavelength. The curves obtained show that, for the implantation and annealing conditions used, substantial shifts in the absorption edge are obtained without drastic modification of the shape of the edge. The short-wavelength limit of the range of measurement (which occurs at 790 nm) is due to the lower limit of the dye laser emission spectrum. Samples implanted with doses in the 10^{15} cm^{-2} range exhibited higher propagation losses.

It was not possible to determine accurate absolute values of the absorption coefficient from the slab waveguide measurements. Instead, absorption coefficients were estimated on three rib waveguide samples: an unimplanted, unannealed control sample, a fluorine IID sample, and a boron IID sample. The IID samples were implanted with doses of 10^{14} cm^{-2} and annealed at 890 °C for 2 and 4 h, respectively. Rib waveguides were defined by dry etching (using $SiCl_4$)

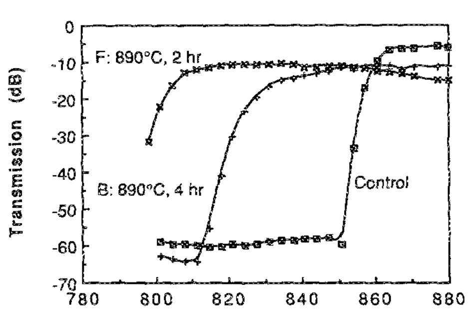

FIG. 3. Optical transmission spectra of IID slab waveguide samples for implantation doses of 1×10^{14} cm^{-2}.

completely through the 0.7-μm-deep disordered MQW layer to leave waveguide ridges 4 μm wide which were multimoded laterally and single moded vertically. The propagation loss was found by measuring the incident and transmitted power of light end-fire coupled using 40× microscope objectives into and out of the waveguides. Because the samples were too short for sequential cleaving the coupling loss was assumed to be 3 dB: a value which accounts for Fresnel reflection losses at the waveguide facets but makes no allowance for modal mismatch. The absorption coefficient values deduced by this method are therefore overestimated. Experimental values of the optical power coupled into and out of the waveguides are given in Table I. The propagation losses were measured at a wavelength of 885 nm in the starting material (7 dB cm^{-1}) in fluorine-disordered material (13 dB cm^{-1}) and in boron-disordered material (22 dB cm^{-1}). The additional losses introduced by the fluorine and boron IID processes were, therefore, estimated to be 6 and 15 dB cm^{-1}, respectively.

These low losses suggest that neutral impurity disordering could become an important process in the fabrication of OEICs. The required annealing conditions (2 h at 890 °C results in a band-gap increase of >60 meV using F) appear to be compatible with retaining good device performance from lasers and modulators: we have subjected a double quantum well laser wafer to an anneal cycle at 905 °C for 2 h and then fabricated the wafer into broad-area lasers. The threshold current density after annealing was 415 A cm^{-2}, the same (to within 5%) as that measured on nonannealed lasers. Work reported with Si IID has used similar annealing conditions: for example, by annealing at 850 °C for 8 h, Thornton *et al.*[5] have fabricated integrated coupled cavity lasers and modulators with laser threshold currents as low as 6.8 mA and modulator depths in excess of 13.6 dB. However, in this case the propagation loss in passive waveguide sections was estimated to be ≈ 71 dB cm^{-1} (17 cm^{-1}) because of free-carrier absorption. Problems which might occur with the redistribution of mobile impurities (such as Zn) during the annealing stage can be minimized by performing a contact diffusion[10] after the disordering process has been completed.

In conclusion, our experiments have shown that both boron and fluorine IID can provide a blue shift in the absorption edge of AlGaAs-GaAs MQW waveguides of up to 100 meV, without a large loss penalty or major increase in the free-carrier density. Evidence of residual damage in both the PL and absorption spectra is seen for ion implantation doses greater than 10^{14} cm^{-2} and, in the temperature range studied, the optimum annealing temperature appears to be 890 °C. The additional absorption loss associated with fluorine disordering is estimated to be only 6 dB cm^{-1}, approximately a factor of 7 lower than the theoretical limit imposed by free-carrier losses with silicon IID. For reasons which are not yet clear, the losses associated with boron IID (15 dB cm^{-1}) represent a less significant improvement. The use of fluorine and boron IID—possibly sequentially and in different regions of a device or in integrated combinations of devices—could have a major impact on the speed of progress towards low-cost monolithic waveguide integrated optoelectronics.

TABLE I. Experimental results of the power coupled into and out of rib waveguides at a wavelength of 885 nm. The propagation loss was calculated by assuming the total coupling loss was 3 dB.

Sample	Power in (mW)	Power out (mW)	Length (mm)	Loss (dB cm^{-1})
Starting material	2.8	1.0	2.0	7.4
Fluorine IID	4.0	1.4	1.2	13
Boron IID	2.6	0.34	2.64	22

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