

ArF laser-based quantum well intermixing in InGaAs/InGaAsP heterostructures

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Radiation from a 193 nm ArF laser was investigated to modify surface properties of InGaAs/InGaAsP quantum well (QW) heterostructures and introduce defects required to enhance intermixing during the annealing process. A top 200 nm thick sacrificial layer of InP served as a reservoir for laser generated defects. The irradiation with up to 90 pulses at 65–150 mJ/cm² allowed to generate an array of 1.2×1 mm² sites of QW intermixed material, with bandgap energy blueshifted up to 107 nm. We discuss the mechanism and advantages of this approach for postgrowth wafer level fabrication of multibandgap QW material. © 2008 American Institute of Physics. [DOI: 10.1063/1.2969063]

Monolithically integrated photonic devices require GaAs- or InP-based wafers with multibandgap structures, the fabrication of which has continuously challenged epitaxial film growers. In an attempt to overcome some of the problems related to the epitaxial growth of such wafers, the post-growth processing quantum well intermixing (QWI) technique has been studied intensively.^{1,2} The underlying idea is to enhance high-temperature intermixing of the barrier and QW materials. This changes confinement profile of the QW and thus, leads to the formation of a different bandgap microstructures. Spatially selective enhancement of the QWI process has typically been achieved by direct doping,³ ion implantation,^{4,5} or by diffusion of surface atoms into a thin layer of film deposited on top of the QW microstructure.^{6,7} However, conventional QWI techniques lack the reproducibility and the reliability required for industrial fabrication of complex multibandgap wafers and a suitable *in situ* monitoring technique has yet to be developed. Excimer lasers are potentially attractive for QWI as they can be used to pattern wafers in numerous sites with different doses of radiation required for point defect generation. Consequently, a multibandgap wafer can be produced in a single rapid thermal annealing (RTA) step.⁸ In addition to the expected enhancement of the intermixing process, we have recently demonstrated that KrF (248 nm) laser irradiation of GaAs based QW heterostructures could also inhibit QWI.⁹ Here, we report on the results of ArF excimer induced QWI in InGaAs/InGaAsP QW heterostructures.

The investigated InGaAs/InGaAsP/InP QW heterostructure was grown by a metal-organic chemical vapor deposition technique on an S-doped InP substrate. It consists of five InGaAs QWs with composition chosen to have material suitable for the fabrication of laser diodes operating at 1.50 μm at room temperature. The 5 nm thick QWs are separated by 12 nm thick InGaAsP barriers. The active region was grown on a 1.4 μm thick buffer layer of n-type (Si, 2×10^{18} cm⁻³) InP and a 130 nm thick n-type (Si, 5×10^{17} cm⁻³) InGaAsP. The top cladding was composed of two Zn-doped layers of InP, 200 and 1200 nm thick, separated by a 10 nm InGaAsP etch stop layer. The contact layer, 100 nm Zn-doped InGaAs, was separated from the cladding

by a second etch stop layer (50 nm) and was covered with a 200 nm thick sacrificial layer of undoped InP. Since bond strength in InP is lower than in InGaAs (Ref. 10) we expect the generation of a high concentration of point defects with relatively low laser fluences in the sacrificial layer. Furthermore, this layer can be selectively etched away after annealing, leaving undamaged InGaAs surface for the fabrication of photonic device on the intermixed material.⁵

We used an ArF excimer laser ($\lambda = 193$ nm) which delivered 15 ns pulses of fluence in the range of 68–150 mJ/cm². The laser beam was homogenized with a double microlens fly eye array and used to project an image of a rectangular mask on the sample surface. With a computer controlled X-Y-Z positioning of the sample, the setup allowed for the processing of the same sample at numerous sites, each measuring approximately 1.2×1.0 mm². The irradiation was carried out in an ambient air environment.

Following the irradiation, the samples were annealed in a RTA furnace under nitrogen atmosphere at 725 °C for 2 min. Since numerous sites of the same sample could be processed with the laser, the annealing conditions were nominally the same for different sites.

Room temperature photoluminescence (PL) measurements were carried out with a commercial mapper (Philips PLM-150) using a Nd:YAG (yttrium aluminum garnet) laser ($\lambda = 1064$ nm) as an excitation source and an InGaAs array detector. The PL maps were created based on spectral position of the QW electron-hole recombination peak, which for the as-grown material was at 1523 nm. The composition of the laser modified surface of InP was investigated with an x-ray photoelectron spectroscopy (XPS) (Kratos HS system) using a monochromatic aluminum $K\alpha$ x-ray source.

Figure 1 shows a PL map of the sample that was irradiated with the ArF laser delivering pulses at 95 and 150 mJ/cm². It can be seen that the formation of an array of clearly distinguishable sites of different bandgap material takes place following the RTA treatment. The upper and lower numbers shown for each site indicate pulse number and amplitude of the blueshift, respectively. For example, it can be seen that the 50 pulse irradiation at 95 mJ/cm² yields the blueshifted by 107 nm (from 1523 to 1416 nm) material. For most of the irradiated sites, the sample shows a reasonable lateral uniformity of the PL emission wavelength, with

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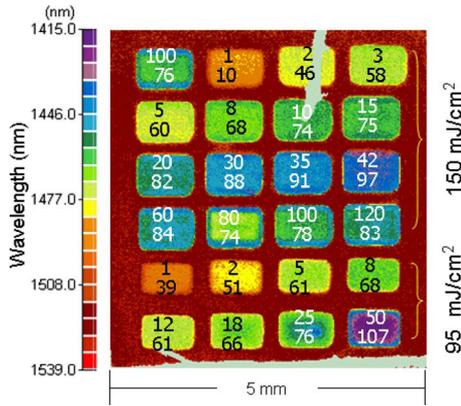


FIG. 1. (Color online) Room temperature PL map of an ArF laser patterned InGaAs/InGaAsP/InP QW heterostructure following the annealing at 725 °C for 120 s. For each site, the upper and lower numbers correspond to the number of laser pulses and blueshift amplitude, respectively.

the standard deviation about 2 nm. Previously investigated irradiation of a similar InGaAs/InGaAsP QW heterostructure with 100 mJ/cm² pulses delivered by a KrF excimer (248 nm) has demonstrated 50 and 25 nm blueshifts achieved with 1000 and 500 pulses, respectively.⁸ The dynamics of the current approach is much stronger and, as it is discussed further in this communication, we could observe significantly greater blueshifts achieved with less than the 80 pulse irradiation.

The formation of a laser generated altered layer, primarily consisting of In_xO_y, has been observed by XPS measurements. Figure 2 shows a series of In 3d_{5/2} XPS spectra taken from sites on the sacrificial layer that were irradiated at 70 mJ/cm² with 10, 50, and 150 pulses. A comparison with the as-grown InP surface clearly indicates the formation of an In_xO_y layer. We have observed that for 90 mJ/cm² and $N > 50$ pulses the oxide layer was thick enough to mask entirely the XPS signal from the bulk InP layer. This indicates that the thickness of the laser created altered layer was at least three times larger than the electron attenuation length in InP, i.e., ~ 2 nm at 1 keV,¹¹ and was comparable to the absorption depth of the 193 nm radiation in InP ($\alpha_{\text{ArF}} = 1.3 \times 10^6 \text{ cm}^{-1}$).¹² The XPS results have also indicated an increase in the In/P signal with the number of irradiating pulses. The photoenhanced reaction with the air environment and photoinduced desorption¹³ are likely mechanisms re-

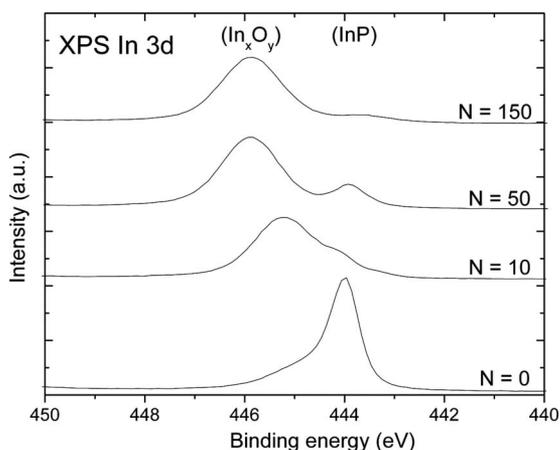


FIG. 2. In 3d_{5/2} XPS spectra of the reference InP sample and ArF laser exposed sites for $N=10, 50,$ and 150 pulses at 70 mJ/cm².

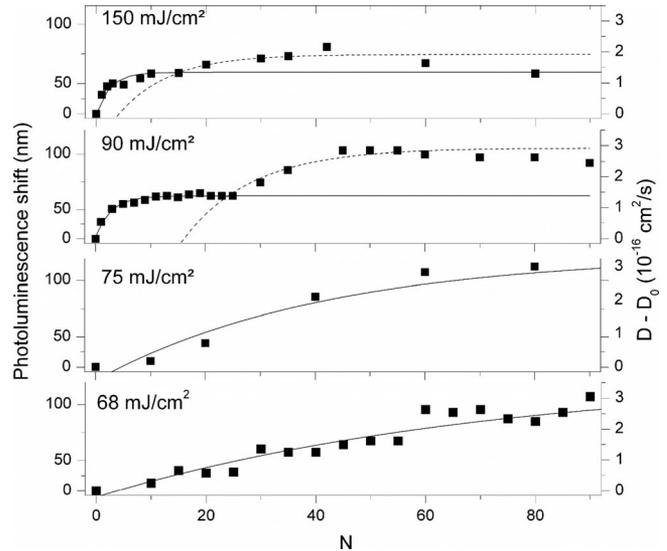


FIG. 3. Dependence of the net blueshift amplitude on the number of ArF pulses delivered at 68, 75, 90, and 150 mJ/cm². Solid lines correspond to the theoretically calculated dependences described by Eq. (1). The last two data points at 150 mJ/cm² were not considered in the fitting procedure.

sponsible for the creation of an altered layer of material, at least for modest laser fluences ($< 90 \text{ mJ/cm}^2$). Current results are consistent with the previously reported formation of a group III-oxide layer on the surface of excimer laser irradiated III-V semiconductors.¹⁴ Also, the formation of a 5.5 nm thick layer of Ga₂O₃ + As₂O₃ was reported on the surface of GaAs irradiated with 1000 pulses of a KrF excimer delivering 100 mJ/cm² per pulse.¹⁵

Figure 3 shows the net blueshift dependence on the number of ArF laser pulses and different pulse fluences observed for the investigated InGaAs/InGaAsP QW microstructure. It can be seen that the blueshift amplitude for 68, 75, and 90 mJ/cm² increases systematically with increasing pulse number and, with the exception of the 150 mJ/cm² data, it has a tendency to saturate at about 100 nm. This suggests that the concentration of defects available for the enhanced intermixing saturates with the increasing dose of laser radiation. The saturation at low laser fluences could be attributed to the complete removal of adatoms¹⁶ and formation of defect clusters that act as traps for point defects, preventing them from diffusing toward the active region and participating in the intermixing process.⁴ Additionally, a reduced efficiency of defect formation could take place due to laser-based formation of an In-rich surface.¹⁷ The results for 90 mJ/cm² ($0 < N \leq 25$) and 150 mJ/cm² ($0 < N \leq 15$) observed in Fig. 3 are likely related to these effects. However, the origin of the step increase in the blueshift amplitudes observed for 90 and 150 mJ/cm², at 25 and 15 pulses, respectively, is less obvious. It appears that at these conditions, defects that enhance the QWI process have been exhausted and formation of a new type of surface defects begins to take place. For instance, it has been reported that the removal of Ga atoms from the GaAs surface is defect initiated and the irradiation with 1.35 eV laser pulses at 400 mJ/cm² could increase and saturate rapidly their removal rate with the pulse number, while for low-fluence pulse irradiation ($\sim 200 \text{ mJ/cm}^2$) such a removal rate decreased and saturated at significantly lower level.¹⁸ It is reasonable to expect that similar effects could be responsible for emission of In

atoms from the InP surface. The reduced amplitude of the blueshift observed for $N > 40$ and $N > 60$ pulses at 150 and 90 mJ/cm², respectively, is likely related to the reduced “reservoir” of laser created defects. Profilometry measurements (not shown) have indicated that at 150 mJ/cm², more than 140 nm of the sacrificial layer was removed with 500 pulses. Following such treatment, we have observed that the blueshift amplitude was reduced by 50% in comparison to its maximum value.

Using a finite element model of the heterostructure, we were able to extract the intermixing coefficient from the PL blueshift. The properties of quaternary materials $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ were extracted using Mei’s interpolation technique¹⁹ assuming they were lattice matched on InP. We also assumed the conservation of the lattice matching in the intermixed material so that $x = 1 - 0.47y$. This assures a maximum 0.032% strain with the InP substrate. Therefore, we can express the QWI process with a single intermixing coefficient, D_{III} . For different diffusion lengths $L_{d_{\text{III}}} = \sqrt{D_{\text{III}}\Delta t}$, where Δt is the diffusion time, the calculation determined the intermixed concentration and energy bands profiles. The RTA experiments carried out for the as-grown material yielded the intrinsic diffusion coefficient, D_0 , equal to $2.1 \pm 0.8 \times 10^{-17}$ cm²/s. This value is almost 50% smaller than $D_0 = 3.7 \times 10^{-17}$ cm²/s observed for a similar material system,²⁰ which suggests a thermally more stable microstructure investigated in this communication. We describe the intermixing process by a phenomenological model of the radiation-assisted diffusion.²¹ In such a case, the intermixing coefficient, D_{III} , is enhanced by the presence of laser created point defects in the QW vicinity, and it can be described by the following formula:

$$D_{\text{III}} = D_0 + \sum_{i=1}^M D_i [1 - e^{-k_i(N - N_{\text{th}_i})}], \quad \text{with } N > N_{\text{th}_1}, \quad (1)$$

where D_i is the defect-enhanced intermixing coefficient, k_i is the pulse dependent rate of defect generation, and N and N_{th_i} are the total and incubation number of pulses, respectively. Experimental data shown in Fig. 3 have been described reasonably well with solid and dotted lines representing a difference between the total and intrinsic intermixing coefficients ($D_{\text{III}} - D_0$). It can also be seen that for 90 and 150 mJ/cm² no threshold for initiation of the blueshift was observed ($N_{\text{th}_i} = 0$). However, four and five pulses were required to initiate blueshifting for fluences of 68 and 75 mJ/cm², respectively. The maximum value of the total intermixing coefficient has been determined to be $D_{\text{max}} = 3.4 \pm 0.4 \times 10^{-16}$ cm²/s. This value is almost seven times smaller than $D_{\text{tot}} = 2.3 \pm 0.4 \times 10^{-15}$ cm²/s that was observed for a similar material system irradiated with a Q-switch Nd:YAG laser.²¹ This difference could be related to the increased thermal stability of our material. The fast dynamics of defect generation with the 193 nm excimer, however, is clearly demonstrated in Fig. 3. It takes less than 100 pulses to saturate the blueshift amplitude, while it required more than 2000 pulses and significantly greater pulse fluences to achieve the blueshift saturation in a similar QW microstructure irradiated with a pulse Nd:YAG laser.²¹ The corresponding defect generation coefficients for the first regime (k_1) are 0.01, 0.02, 0.35, and 0.39 for 68, 75, 90, and 150 mJ/cm², respectively. For 90 and 150 mJ/cm², k_2 values are 0.08 and

0.11, respectively. A reduced maximum value of the total intermixing coefficient $D_{\text{max}} = 1.92 \pm 0.02 \times 10^{-16}$ cm²/s that was obtained for 150 mJ/cm² is likely related to the mentioned earlier partial removal of the sacrificial layer. In comparison to the pulsed Nd:YAG laser experiments,²¹ our results showed drastically increased rates of defect formation.

In summary, we have investigated a 193 nm ArF excimer laser defect formation in the sacrificial layer of InP, deposited on top of InGaAs/InGaAsP QW heterostructures, as a means to enhance the QWI process. The net blueshifts of up to 107 nm have been observed for irradiation with laser pulse fluences below 90 mJ/cm². For higher fluences, defect-mediated surface atom removal and “soft” ablation of the sacrificial layer could be responsible for the appearance of the two-step saturation observed in the blueshift amplitude. The quantitative description of the mechanisms involved in this ArF laser induced QWI process still requires detailed analysis, however, our results have already indicated the control level of the QWI process and flexibility in the fabrication of multibandgap QW wafers that cannot be matched by other known QWI techniques.

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