Controlled intermixing in InGaAsP multiquantum wells by plasma immersion ion implantation of argon

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Abstract

In this paper, the diffusion enhanced intermixing effect in strained InGaAsP multiquantum wells due to plasma immersion ion implantation (PIII) of Ar⁺ and post-implant annealing is presented. Firstly, we report that a 20 kV Ar⁺ PIII at a fluency of 10¹⁶ cm⁻² together with a furnace anneal at 650°C resulted in an enhanced blue shift in the photoluminescence (PL) peak. It was also found that by varying the Ar⁺ dose or the implantation energy, we could control the extent of the implantation induced intermixing. For a sample that had half of the surface shielded during implantation, a bandgap step was observed between the implanted and non-implanted regions. Our results indicate that one can use this technique for localised fine-tuning of the bandgap energy, thus demonstrating its potential as a processing step for the fabrication of integrated photonic devices.

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1. Introduction

Recent developments in the optoelectronics devices have generated much interest in the research of semiconductor multiquantum well (MQW) materials with tunable bandgap in selected area within the same substrate. Various techniques, including selective area growth and the use of patterned substrate [1], have been used for introducing localised variation of bandgap in the MQW wafer. However, since these techniques require the wafer to go through additional growth steps, they tend to introduce unwanted growth defects, which eventually lead to poor device yield. Quantum-well intermixing (QWI) is a simple and practical technique for modifying the quantum well (QW) bandgap energy. Photoabsorption-induced intermixing (PAID) [2,3], impurity free vacancy disordering (IFVD) [4,5] and ion...
implantation induced QW composition disordering (IID) \cite{6,7} are a few examples of the selective techniques that have been reported. More recently, we have demonstrated that plasma immersion ion implantation (PIII) \cite{8} can also induce QW disordering. In comparison to IID using conventional beam-line machines, which is a "line-of-sight" DC implantation, MQW intermixing using PIII has the advantage for treating large, non-planar and batch samples due to the fact that the plasma beam is a much more uniform ion source and there is no directional dependence. In addition, since PIII is essentially a "pulsed" process in which the ion dosage and implantation energy can be easily changed by varying the pulse width and pulse profile, one can quite conveniently control the extent of intermixing by varying these two parameters.

In this paper, we present results on the spatially selective intermixing of InGaAsP MQW structure using PIII of low-energy Ar$^+\$. We also demonstrate that by varying the implantation dosage or ion energy, the bandgap shift in the MQW structure can be controlled.

2. Experimental

The materials we used was a nominally undoped 1.3 $\mu$m MQW structure containing seven 60 Å compressively strained InGaAsP wells and six 100 Å InGaAsP barriers bounded by two InGaAsP confinement layers. The In/Ga ratio was constant throughout the MQW structure. The cap and buffer layers were 450 nm thick p-InP and 2 $\mu$m n-InP, respectively. The epilayers were prepared by metal organic vapour phase epitaxy (MOVPE). Room temperature photoluminescence (PL) was used to find the emission peak of the MQW samples. A 5 mW He–Ne laser was used as the excitation source and a liquid nitrogen cooled Ge photodiode as the PL signal detector. In the actual experiment, the samples were first cleaned in acetone, then PIII treated and finally annealed to give the desired intermixing effect. PIII was performed at 20 kV with Ar$^+$ dose ranging from $10^{13}$ to $10^{16}$ cm$^{-2}$. The base pressure in the PIII chamber was $2 \times 10^{-1}$ Pa. Standard furnace annealing and rapid thermal annealing were carried out for 30–90 min at 650°C and 2–4 min at 700°C (or 650°C in some cases), respectively. All annealing experiments were conducted in a flowing nitrogen atmosphere and with the sample sandwiched between two slices of silicon to suppress phosphorus evaporation.

Also, the PIII experiments were performed using different implantation voltages with the Ar$^+$ dose kept constant at $10^{13}$ cm$^{-2}$. The implantation voltages were 20, 30, 40 or 50 kV. Post-implant RTA was performed at 650°C for 2–6 min. This temperature was lower than that used in the previous experiment because we found that for high implantation energies, RTA at 700°C gave very weak PL signals.

To demonstrate the spatially selective intermixing by PIII, one of the samples had half of its surface shielded by a slice of pure InP during PIII of Ar$^+\$. The PIII dose and energy were $10^{16}$ cm$^{-2}$ and 20 kV, respectively. The furnace anneal was performed at 650°C for 90 min.

3. Results and discussions

As shown in Fig. 1, the sample that had been implanted by a dose of $10^{16}$ cm$^{-2}$ Ar$^+$ at 20 kV and subjected to a post-implant furnace anneal clearly exhibits an extra blue shift in comparison to the non-implanted control sample. A maximum of 20 nm blue shift in the PIII treated sample has been observed. To explain our observation, we treat the annealing processing as the promotion of a thermally activated reaction such as re-crystallisation or diffusion. In our furnace anneal, the reaction takes place under homogenous and isothermal conditions, and the diffusion coefficient follows the Arrhenius law

$$D = D_0 \exp(-Q/kT),$$

where $T$ is the anneal temperature, and $Q$ is the activation energy required for an atom to jump from one stable position in the crystal to the next. Since our samples have constant Group III contents throughout the MQW region, only Group V atoms can diffuse. For a given temperature, the
di/C128usion process is primarily due to the di/C128usion of group V atoms and is governed by a constant satisfying the Arrhenius law. In the present case, the di/C128usion coefficient is obtained by using the technique described by Li et al. [14]. This tech-nique assumes that initially the interfaces within the MQW structure have abrupt compositional steps. When intermixing occurs, the bound energy states in the QWs undergo blue shift. The measured blue shift can be used directly for calculating the composition profile of the MQW structure. This in turn allows us to estimate the di/C128usion coefficient of the constituent atoms. At the an-nealing temperature of $T = 923$ K, the fitted average di/C128usion coefficients of group V atoms in the non-implanted and implanted samples are $2.5 \times 10^{23}$ and $1.0 \times 10^{22}$ m$^2$s$^{-1}$, respectively. Thus, the conditions used for the current PIII resulted in a factor of four increase in the di/C128usion coefficient.

In the second experiment, we demonstrate that the intermixing effect can also be controlled by amount of Ar$^+$ implanted into the sample. The MQW samples were PIII at 20 kV with Ar$^+$ dose ranging from $10^{13}$ to $10^{16}$ cm$^{-2}$. RTA was performed at 700°C for 2–4 min. Fig. 2 shows the
subsequent PL blue shifts of the samples. Since RTA is essentially a transient process in which the diffusion speed increases rapidly as the anneal progresses, the derivation of diffusion coefficients from the data is aimed to give only an estimate of the average diffusion coefficient of group V atoms for our experiments. The average diffusion coefficient shows a steady increase from $9.4 \times 10^{22}$ to $17.0 \times 10^{22}$ m$^2$ s$^{-1}$ as the implantation dose is increased from $10^{13}$ to $10^{16}$ cm$^{-2}$.

Apart from varying the Ar$^+$ dosage, the effect of intermixing can also be controlled by changing the implantation energy. Fig. 3 shows the evolution of the PL blue shift as the implanted samples went through RTA at 650°C from 2 to 6 min. The general trend observed from Fig. 3 is that as the implantation energy increases from 20 kV through to 50 kV in steps of 10 kV, the intermixing effect, as indicated by the PL blue shift, also increases. This observation is true except for one data point, which was obtained from the sample that underwent 40 kV PIII and annealed for 4 min. The PL peak shows a smaller than expected blue shift in comparison to other samples. Since the accuracy of the PL peak measurement was within 0.5 nm, the deviation is too large to have been caused by measurement error. During the experiment, the implantation dose was estimated by noting the current pulse duty cycle and the total implantation time so that the total ion count could be read directly from a calibrated chart. In addition, the plasma shroud covered an area much larger than that of the sample. All the samples were PIII treated in batches prior to the final RTA process. It is, therefore, unlikely that implantation variations due to inhomogeneity within the plasma shroud or run-to-run drift would have led to the unexpected variation in PL blue shift. We believe that the possible reason behind this discrepancy can be related to an unexpected change of RTA temperature caused by residual surface stain left on the sample after solvent cleaning or epitaxial growth variation across the wafer. Another point worth mentioning is that the detected PL signal from the sample implanted at 50 kV produce a PL signal about 100 times weaker than that of a non-implanted sample. It was for this reason that we had to use 650°C instead of the original 700°C, which gave too weak a PL signal for obtaining reliable data.

Fig. 4 shows the scanning PL plot obtained from the sample that had half of its surface masked by a piece of InP during PIII. The PL peak wavelengths were measured from the non-implanted to implanted regions. It can be seen that the implanted region clearly shows an extra blue shift of 16–18 nm. The coarse spatial resolution of the PL measurement at around 250 µm was due to the large spot size of the pump laser source in the PL spectrometer. Our results have nevertheless demonstrated that one can perform selected area disordering using the PIII technique.
As a basis for explaining our results, we believe that the observed intermixing is primarily attributed to the diffusion of point defects generation by ion bombardment. As shown in Fig. 5, high-resolution cross-sectional transmission electron microscopy reveals the surface of the as-PIII treated sample that contains a large amount of point defects. The region within a thickness of about 200–300 Å from the surface has become almost amorphous. In the context to ion implantation in relation to intermixing, our observation is similar to that reported by Oshinowo et al. [9]. Upon annealing, the material re-crystallises through re-absorption of the point defects. This region serves as a diffusion source from which point defects are driven into the bulk of the sample. When re-absorption takes place between the diffusing point defects and the host atoms in the MQW region, intermixing occurs. The effect of intermixing would increase if a larger concentration of defects were diffusing through the MQW region. We believe this to be the reason leading to the present result that intermixing effect increases with Ar⁺ dosage and implantation energy. High Ar⁺ implantation doses will produce a high defect concentration and, hence, there will be more defects available for inducing MQW intermixing. For the energy case, higher implantation energy will lead to deeper penetration of the Ar⁺ ions and hence
thicker defect-rich region. This also means that the source of the defect source will be closer to the MQW region and, thus, there would be better chance for point defects to reach the MQW material to induce intermixing before being re-absorbed by the surface region. Paquette et al. [10] also reported similar intermixing results when they implanted a 1.55 μm laser structure based on the compressively strained quaternary InGaAsP/InGaAs/InP material system using low-energy (18 keV) implantation of As\(^{+}\) at a dose of \(1 \times 10^{12}\) cm\(^{-2}\). Upon RTA at 685°C for 60 s, the sample showed an extra 14 nm blue shift. Another experiment demonstrating similar result was performed by Poole et al. [6]. They ion implanted an InGaAsP/InGaAs MQW laser structure with high-energy (1 MeV) P\(^{+}\) ions at a dose of \(2.5 \times 10^{13}\) cm\(^{-2}\). RTA at 700°C for 90 s gave a 60 nm blue shift. Though the implantation energy and species were different, both experiments revealed that point defects, probably in the form of vacancies, created by ion implantation of the group V host atoms (As, P) would diffuse and induce intermixing and bandgap widening during post-implantation anneal [11]. This is confirmed by our results, since Ar is electronically neutral in the MQW material, the intermixing effect is not due to the diffusion of active impurities such as Zn or Si [12,13], but diffusion of implantation defects, similar to that proposed for the cases of As\(^{+}\) and P\(^{+}\) implantation, is most likely the main reason behind the observed intermixing effect. The PIII step in effect generates a high density of point defects at the surface layer of the structure. Upon thermal annealing, the defects in the implanted region can be driven into the MQW via diffusion. The MQW then become intermixed due to the interlattice exchange of host atoms via defect sites.

In addition to providing a better understanding of intermixing mechanism, the present study also demonstrates a more important aspect associated with the PIII approach. That is, in comparison to conventional beam-line implantation, PIII offers the advantage of relatively more precise control on the intermixing by continuously varying the ion dose and energy during implantation.

4. Conclusions

In summary, we have shown the enhanced intermixing effect in compressively strained InGaAsP MQW structures by low-energy PIII of Ar\(^{+}\) ions and thermal anneal. By varying the ion dosage or the implantation energy, one can control the extent of intermixing. In addition, we have also shown that selected area intermixing can be achieved by masking the surface from the implantation. Our results suggest that this technique can be used for fabrication of photonic devices.

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