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Citation	Xu, C. D., Mei, T., Nie, D., & Dong J. R. (2006). Halftoning band gap of InAs/InP quantum dots using inductively coupled argon plasma-enhanced intermixing. Applied Physics Letters, 89, 1-3.
Date	2006
URL	http://hdl.handle.net/10220/6409
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Halftoning band gap of InAs/InP quantum dots using inductively coupled argon plasma-enhanced intermixing

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(Received 4 July 2006; accepted 3 August 2006; published online 25 September 2006)

Inductively coupled argon plasma-enhanced intermixing of InAs/InP quantum dots grown on InP substrate is investigated. Intermixing is promoted by the near-surface defects generated by plasma exposure in annealing at a temperature of 600 °C for 30 s. The annealing results in a maximum differential band-gap blueshift of 106 nm but a thermal shift of only 10 nm. Band-gap halftones are obtained by controlling the amount of near-surface defects via wet chemical etching on the plasma-exposed InP cap layer. No degradation of quantum-dot crystal quality due to the process has been observed as evidenced by photoluminescence intensity.
[DOI: 10.1063/1.2357563]

Self-organized semiconductor quantum-dot (QD) structures have recently been a subject of extensive research due to their attractive properties for making high performance optoelectronic devices.[1] InAs/InP QD grown on InP substrate is of particular interest as its emission wavelength at room temperature can be tuned to ~1.55 μm for optical telecommunication applications.[2] As an essential requirement for monolithic integration of optoelectronic devices on a single chip as a photonic integrated circuit (PIC), selective and controllable band-gap modification has also to be achieved in InAs/InP QD-based structures. Several techniques for quantum-dot intermixing (QDI), such as laser-induced disordering,[3] impurity-free vacancy-induced disordering (IFVD),[4,5] and ion-implantation-induced disordering,[6] have been effectively applied to In(Ga)As/GaAs QD structures. Comparatively, intermixing of InAs/InP QD structures is far more challenging. IFVD has been reported to tune the band-gap energy of an InAs/InP QD structure,[7] whereas the relatively high annealing temperature required for activating intermixing leads to a large amount of unwanted thermal shift on unintended regions, owing to the large surface area to volume ratio of QDs and the poor thermal stability of InP-based materials.[8] The large thermal shift results in a reduced differential band-gap blueshift and thus reduced band-gap tuning range. A practical method to reinforce the thermal stability of InAs/InP QDs is to insert a thin GaAs interlayer to reduce As/P exchange as adopted in the work of proton implantation-induced intermixing.[9]

The inductively coupled argon plasma-enhanced intermixing technique has achieved large differential band-gap blueshift with negligible thermal shift in an InGaAs/InP quantum well (QW) structure.[10] In this letter, we investigate the band-gap modification of an InAs/InP QD structure using the inductively coupled argon plasma-enhanced intermixing. This technique utilizes mobile point defects generated at the near-surface region during plasma exposure to promote intermixing at relatively low annealing temperature and thus there is no appreciable thermal shift as encountered in other techniques.[7,9] The accumulation of near-surface defects due to plasma exposure is studied using x-ray photoelectron spectroscopy (XPS). Band-gap halftoning is realized by controlling the amount of mobile point defects using wet chemical etching to partially remove the plasma-exposed InP cap.

The InAs/InP QD structure used in this study was grown by metal-organic chemical vapor deposition on an InP (100) substrate. The growth conditions have been detailed in Ref 7. The 5 ML InAs dot layer was deposited at 480 °C, while the 100-nm-thick InP buffer layer and the 1-μm-thick InP cap layer were grown at 610 °C. The emission peak from the ground state of the InAs/InP QD is around 1310 nm at 77 K, which is significantly shorter than the normal value, possibly due to the As/P exchange during the long time growth of the 1-μm-thick InP cap layer.[11] The argon plasma exposure was carried out using an ICP180 plasma source generator at varied rf power and inductively coupled plasma (ICP) power, while the argon flow rate and the chamber pressure were fixed at 100 SCCM (SCCM denotes cubic centimeter per minute at STP) and 60 mTorr, respectively. The annealing was performed at 600 °C for 30 s under flowing N_2 ambient using InP proximity caps. Photoluminescence (PL) spectra were measured at 77 K using a green crystal laser (532 nm, ~25 W/cm^2) for excitation.

Figure 1 shows the plot of band-gap blueshift versus plasma exposure time for samples exposed to argon plasma at 200 W rf power and 500 W ICP power after annealing. The level of thermal shift obtained from an unexposed and annealed-only sample is also marked for reference. The band-gap blueshift increases at the initial stage due to accumulation of point defects in the near-surface region and slightly decays for long plasma exposure duration. The process has achieved a band-gap blueshift greater than 100 nm, or equivalently a differential band-gap blueshift greater than 90 nm by taking into account the thermal shift of only 10 nm. This small thermal shift is ascribed to the relatively low annealing temperature, which is the lowest among those ever reported for defect-enhanced QDI process.[3–7,9]

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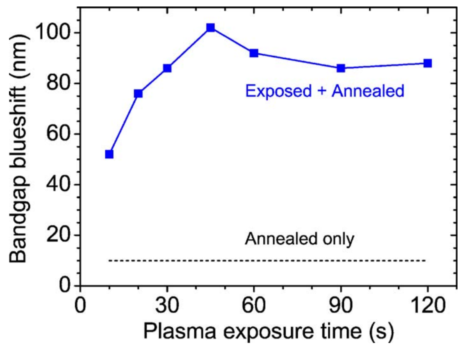

FIG. 1. (Color online) Band-gap blueshift vs Ar plasma exposure time for samples being exposed and annealed. The level of thermal shift is obtained from an annealed-only sample.

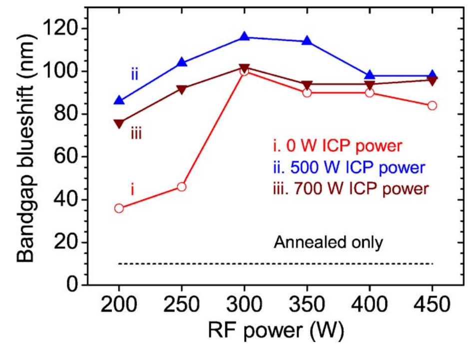

FIG. 3. (Color online) Band-gap blueshift vs rf power under (i) 0 W ICP power, (ii) 500 W ICP power, and (iii) 700 W ICP power. The plasma exposure time was fixed at 30 s.

Ion bombardment during plasma exposure may lead to the compositional change and a highly dense defect structure in the near-surface region of the InP layer. P atoms can be preferentially sputtered from InP due to the mass difference between the In and P atoms with the surface binding energies of secondary importance.[12] In an XPS analysis (using a monochromatic Al $K\alpha$ x ray as excitation source) of one as-grown and two plasma-exposed (1 and 2 min, respectively) samples, by normalizing the counts from the In 3*d*5 and P 2*p* core levels of the plasma-exposed samples as labeled in Fig. 2 to those of the as-grown sample, the surface composition of the InP layer alters to $In_{0.51}P_{0.43}$ and $In_{0.388}P_{0.375}$ with the P/In ratio changing to 0.84 and 0.97 after 1 and 2 min exposures, respectively. The surface composition of the InP layer is governed by an interplay of several competing processes, mainly preferential sputtering and radiation-enhanced diffusion and segregation,[13] whereas it has not reached the equilibrium state within the plasma exposure times employed in the experiment (see Ref. 12 as a reference). The experimental evidence of P deficiency and the correlation between the reduction of P deficiency and the slight decay of band-gap shift shown in Fig. 1 for longer plasma exposure collectively indicate that P vacancies are the dominant defects responsible for promoting the intermixing.

The effectiveness of the inductively coupled argon plasma-enhanced intermixing technique for InAs/InP QD structures can be seen from the achieved large differential band-gap blueshift with small thermal shift, in contrast to the results reported in Ref. 7 where the IFVD technique was adopted and the differential band-gap blueshift was significantly reduced by the large thermal shift in a similar InAs/InP QD structure. We ascribe the large differential band-gap blueshift mainly to the separation of the two processes for defect generation and defect diffusion for promoting intermixing. A large amount of mobile point defects, dominantly the P vacancies, has already existed after plasma exposure without a demand on annealing temperature such that intermixing can be promoted in annealing at a relatively low temperature. However, in the IFVD technique, defects first have to be generated, requiring a higher temperature than is desirable, hence increasing the thermal intermixing process. As a result, significant thermal shift is induced on unintended sections. The issue is more critical for the case where the materials have less thermal stability, such as InAs/InP QDs.

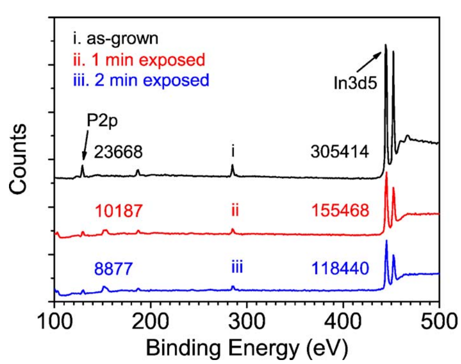

FIG. 2. (Color online) XPS spectra measured from the InP cap layer for (i) as-grown sample and samples exposed to Ar plasma for (ii) 1 min and (iii) 2 min. The counts from In 3*d*5 and P 2*p* core levels for the three samples are labeled as well.

In an ICP system, the rf power and ICP power collectively determine the ion energy and ion density in the plasma and thus the amount of mobile point defects generated at the near-surface region. To maximize the amount of mobile point defects and thus the achievable band-gap blueshift, the rf power and ICP power have been further optimized. Figure 3 shows the band-gap blueshifts for samples exposed to argon plasma for a fixed duration of 30 s at varied rf powers and three ICP power levels. The curves reach their maxima at 300 W rf power and different ICP power levels, whereas the maximum blueshift is obtained at 500 W ICP power (for clarity the data for 300 W ICP power are not plotted). The decreased band-gap blueshift at high rf or ICP power might be caused by the increased sputter rate, leading to effective etching of the InP cap layer and removal of the near-surface defects.[14] A maximum band-gap blueshift of 116 nm or equivalently a differential band-gap blueshift of 106 nm is achieved at 300 W rf power and 500 W ICP power after optimization.

For monolithic PIC applications, it is important not only to selectively alter the band-gap on intended areas but also to halftone the band gap into several levels to satisfy band-gap energy demands of various types of devices, such as emitter, modulator, and waveguide. In several approaches,[10,15] the plasma-enhanced intermixing technique can control the amount of surface point defects laterally to obtain multi-levels of band gap in QW structures. In this work, we use wet chemical etching to remove defects partially from the InP cap such that defect creation, defect amount control, and intermixing promotion by defects become three thoroughly independent processes. A piece of the substrate was firstly covered by a 300 nm SiO_2 layer prepared by plasma-

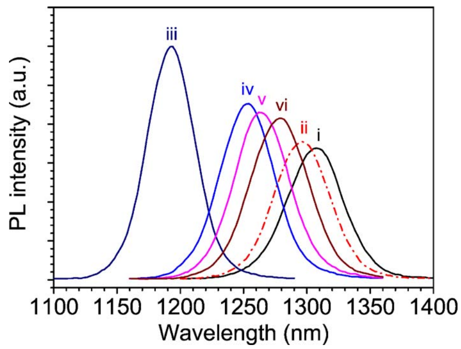

FIG. 4. (Color online) PL spectra measured at 77 K from (i) an as-grown sample, (ii) a sample exposed to argon plasma and annealed with a 300-nm-thick SiO_2 layer (SiO_2 layer was removed before PL measurement), and bare samples exposed to argon plasma, chemically wet etched in $HCl:H_2O$ (1:2) solution for (iii) 0 min, (iv) 3 min, (v) 5 min, and (vi) 7 min, and finally annealed.

enhanced chemical vapor deposition, which is thick enough to block the plasma bombardment effect,[10] and then divided into several samples. The SiO_2 layer was reserved on one sample only and removed in diluted HF solution for the rest of the samples. All samples were exposed to argon plasma for 30 s under 300 W rf power and 500 W ICP power, and subsequently the bare samples were chemically wet etched for different time durations in $HCl:H_2O$ (1:2) solution with an etch rate of ~10 nm/min. Finally all samples were annealed at 600 °C for 30 s in one run and their measured PL spectra are shown in Fig. 4. The 10 nm blueshift from the SiO_2 covered sample is just the same as the thermal shift marked in Fig. 1, showing that the SiO_2 layer completely prevents defect generation by plasma exposure and also the annealing temperature is too low to cause IFVD effect. Subject to different etching times and thus depths, the emission peaks from the exposed and etched samples lie between the thermally shifted and completely shifted peaks, showing halftones of band gap due to effective control on the amount of point defects by wet chemical etching. The wet chemical etching itself brings negligible amount of defects, as being verified from an unexposed sample subject to wet chemical etching for 5 min which showed only thermal shift. In addition, there is no crystal quality degradation caused by the process as evidenced by the preserved PL intensity.

In summary, inductively coupled argon plasma-enhanced intermixing has been shown to modify the band-gap energy of InAs/InP QDs effectively. A maximum differential band-gap blueshift of 106 nm has been obtained with a thermal shift of 10 nm only. The QDI can be done selectively using a SiO_2 layer as the plasma exposure mask, whereas band-gap halftones can be obtained by controlling the amount of introduced defects in the InP cap via wet chemical etching. The QD crystal quality is not degraded in the process as evidenced by the preserved PL intensity. Defect creation, defect amount control, and intermixing promotion by defects are implemented in independent processes, which are practically advantageous for process control in device fabrication.

The authors gratefully acknowledge the financial support (research Grant No. ARC 2/05) from the Ministry of Education (MOE) and the Agency for Science, Technology and Research (A*STAR), Singapore.

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