

# Band gap blue shift of InGaAs/InP multiple quantum wells by different dielectric film coating and annealing

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## Abstract

Band gap blue shift of InGaAs/InP multiple quantum well (MQW) structures by impurity-free vacancy disordering (IFVD) is studied by photoluminescence (PL) and secondary ion mass spectrum (SIMS). SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, and spin on glass (SOG) were used for the dielectric layers to create the vacancies. The results indicate that the band gap blue shift varies with the different dielectric layers and depends on the annealing temperature. The blue shift is also related to the combination of the layers between dielectric and cladding layers. The SIMS profile shows that the dielectric capped layer and rapid thermal annealing caused the quantum well intermixing, which results in the band gap blue shift. Optimum condition can be reached by choosing suitable dielectric layer and annealing condition.

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## 1. Introduction

Photonic and electronic integrated devices based on InGaAs(P)/InP multiple quantum well (MQW) structures are attracting much attention for optical communication system development [1–6]. Selective band gap tuning is crucial in fabricating these integrated photonic devices. For achieving this goal, different techniques are currently under investigation, including selective area growth and growth–etch–regrowth. Regrowth requires many steps of etching and regrowth is often associated with low efficiency and poor yield [7]. Also, the contamination and defects at the etching and regrowth interface are difficult to avoid. Quantum well intermixing (QWI) technology has shown as a good way to achieve this purpose for high power semiconductor lasers and photonic integrated devices and

circuits [5,6,8]. QWI is based upon the post-growth tuning of band gap energy of multi-quantum well (MQW) structures to avoid the complicated post growth processing. In order to realize the monolithic integration of active and passive optoelectronic devices and components, as an alternative approach, post growth QWI becomes a more attractive technique, which can change the QW shape and composition by intermixing wells and barriers in QWs and gives rise to a blue-shifted band gap. This post-growth control of QW profiles or the post-tuning of optical band gap energy can be realized by impurity-induced intermixing or impurity-free vacancy enhanced intermixing [5,6,8,9]. Several technical approaches have been explored to achieve this purpose, including impurity-induced disordering (IID) [10,11], implant-induced composition disordering (IICD) [7,12–14], and impurity-free vacancy disordering (IFVD) [7,15–17]. IID usually introduces some free carriers, which usually cause absorption. IICD creates some defects by ion implantation damaging the crystal quality and it also needs high energy implanter to perform the ion implantation for

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actual laser structure because of thick clapping layer. In comparison with IID and IICD, IFVD shows to be more promising because it can keep high crystal quality and low optical propagation losses as well as not introduce free carrier concentration. In the approach of IFVD, utilizing a dielectric layer as Ga sink at elevated temperature results in the redistribution of Ga vacancies in MQW structures to enhance quantum well intermixing [18,19]. So, IFVD is a simple effective approach to create band gap tailing without free carrier adsorption and damage of crystal lattice.

During the IFVD process, there usually involves a deposition of a dielectric capping layer such as  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  on the top of QWs and a rapid thermal annealing (RTA) at elevated temperature. Vacancies can be created at the dielectric–semiconductor interface due to the out-diffusion, for example, Ga atoms from the semiconductor layers into the dielectric region. The diffusion of these vacancies into the structure can enhance the QW intermixing, leading to a large blue shift of the QW band gap with minimum effect on their electrical and optical properties [19,20]. By using the IFVD technique, QW intermixing has been realized on multiple quantum well (MQW) structures of InGaAs/InP [6,7,15], InGaAs/GaAs [16,17], AlGaAs/GaAs [16], InGaAs/InGaAsP [7], and InGaAsP/InGaAsP [21].

It is found that the choice, combination and properties of capping layers have important influence on the degree of QWI and band gap blue shifts. The  $\text{SiO}_2$  dielectric cap is porous to out-diffusion of Ga atoms, so generating group III vacancies that result in diffusion of Group III atoms from the barrier to the well [22]. As a result, effective band gap of the QW is widened. If the cap does not absorb significant Ga atoms, QWI is suppressed. For the GaAs–AlGaAs QW system,  $\text{SiO}_2$  cap has been generally used to promote QWI while  $\text{SiN}_x$  is used as a mask to prevent or suppress QWI because  $\text{SiO}_2$  cap layer induces a relatively larger blue shift than  $\text{SiN}_x$  cap layer [23]. A very thin  $\text{SiO}_2$  cap is also expected to suppress QWI because of saturation of Ga absorption [24].

For the InGaAs/InP system,  $\text{SiO}_2$  cap is also employed to enhance QWI while  $\text{Si}_3\text{N}_4$ ,  $\text{Ga}_2\text{O}_3$ , P:SiO<sub>2</sub>, and SrF<sub>2</sub> are used to suppress the intermixing [17]. By changing the deposition pressure of  $\text{SiO}_x$  capping layers, variable blue shifts can be obtained [17]. It is also reported for this system that the  $\text{SiO}_2$ – $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$  combination produces the band gap blue shift while  $\text{SiO}_2$ –InP or  $\text{SiN}_x$ –InGaAs cap layer combinations did not show significant energy shift [15]. The effect of semiconductor–capping layer combination on QWI for the  $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{In}_{1-x}\text{Ga}_x\text{As}_{1-y}\text{P}_y$  MQW structures showed similar trends [7]. The samples with the InGaAs/ $\text{SiO}_2$  capping layer combination exhibited a higher degree of intermixing than those with the InP/ $\text{SiO}_2$  capping layer combination after RTA treatment. This is attributed to the fact that InP has no Ga atom and possesses a lower thermal expansion coefficient than InGaAs [7].

However, the reliability and the mechanism of IFVD still need further investigation to meet the requirement of device processing.  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  as dielectric layer in IFVD have

been reported in AlGaAs/GaAs and InGaAs/InP systems, respectively [6,9]. However, to our knowledge, there is no report on the comparison between these two dielectric and spin on glass (SOG) layer used in InGaAs/InP system.

In this paper, systematic investigation on band gap shift of InGaAs/InP system using  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ , and SOG as dielectric layers in IFVD is reported. The mechanism of the quantum well intermixing is discussed based on PL and SIMS analysis.

## 2. Experimentals

$\text{In}_{0.65}\text{Ga}_{0.35}\text{As}/\text{InP}$  lattice matched multi-quantum well (MQW) structures were grown by gas source molecular beam epitaxy (GSMBE). Four 7.5 nm InGaAs quantum wells separated by 10 nm InP barriers were grown on semi-insulating (SI) InP substrate and capped with 50 nm InP layer which can allow the radiation from wells to penetrate through. Therefore this structure is suitable for PL study. The structure and the band gap are shown in Fig. 1.

All samples were cleaved into  $2 \times 3 \text{ mm}^2$  for PL measurements and  $5 \times 6 \text{ mm}^2$  for SIMS profile characterization. The samples were divided into three groups of capped dielectric layers of  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$  by plasma enhanced chemical vapour deposition (PECVD) and SOG (spin on glass) by spin coating at 3000 rpm for 20 s. The thickness of the dielectric layer in all samples is about 150 nm. For the SOG capped samples were then backed at 350 °C for 2 h under pure nitrogen ambient protection.

The samples were then annealed in a rapid thermal annealing (RTA) furnace at the temperature range from 600 to 850 °C in 50 °C steps. The annealing time for all samples was kept for 10 s in accordance with our previous studies [6]. During the RTA the samples were covered with a piece of SI–GaAs face-to-face to minimize the decomposition of InP and possible contamination. All annealing processes are under pure nitrogen protection.

Photoluminescence (PL) measurements were performed at the temperature range from 10 K to 300 K. The excitation source was an argon laser with the wavelength of 488 nm. The secondary ion mass spectroscopy (SIMS) profile was carried out utilizing a SIMS instrument in mode of IMS-6F made in France. Cs ions were utilized as primary beam. In, Ga, and As ions were detected at the depth by  $\text{Ar}^+$  beam sputtering.

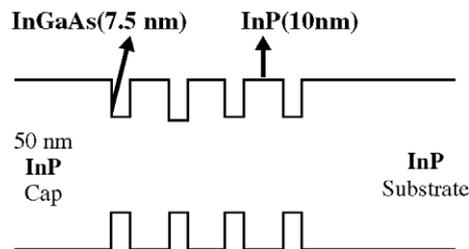


Fig. 1. The structure of experimental samples.

### 3. Results and discussion

The results of PL spectra and SIMS characterization for the samples with three kinds of capped dielectric layer are discussed as follows.

#### 3.1. Si<sub>3</sub>N<sub>4</sub> covered sample

The PL spectra of InGaAs/InP MQW structures capped with Si<sub>3</sub>N<sub>4</sub> and annealed at temperature of 800 °C for 10 s compared with the control sample and annealed only sample as well as those by SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, and SOG covered IFVD are shown in Fig. 2. It can be observed that the PL peak of the sample coated with Si<sub>3</sub>N<sub>4</sub> annealed at 800 °C for 10 s shifts 16 meV towards short wavelength. However, the PL peak of the sample without Si<sub>3</sub>N<sub>4</sub> capping shifts only 3 meV, indicating that the InGaAs/InP structure at 800 °C is thermal stable and the Si<sub>3</sub>N<sub>4</sub> capping layer created some vacancies which result in the Ga and As redistribution. This quantum well intermixing caused the band gap blue shift.

In order to find the temperature dependence of band gap blue shift, the samples covered with Si<sub>3</sub>N<sub>4</sub> were annealed at temperatures of 600, 650, 700, 750, 800, and 850 °C, respectively. Fig. 3 shows the temperature dependence of band gap shift. It can be observed that the shift of PL peak increases with the rising of the RTA temperature. For low temperature range, 600–700 °C, the PL peaks experienced only little change; however, when the annealing temperature went over 700 °C, the PL peak moved to short wavelength evidently. At 750 °C, it shifted 12 meV, at 800 °C it shifted 16 meV and at 850 °C, the blue shift reached 30 meV. However, the surface morphology at 850 °C became rusty due to the P-decomposition from InP. Taking account of this effect, annealing at 800 °C is probably the optimum condition under which 16 meV blue shift can be obtained, and at the same time, the surface of the sample kept good quality morphology.

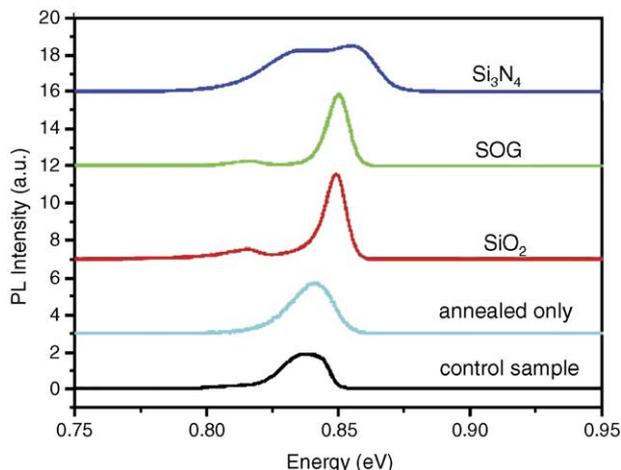


Fig. 2. The PL spectra of control sample and annealed only sample as well as those by SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, and SOG covered IFVD.

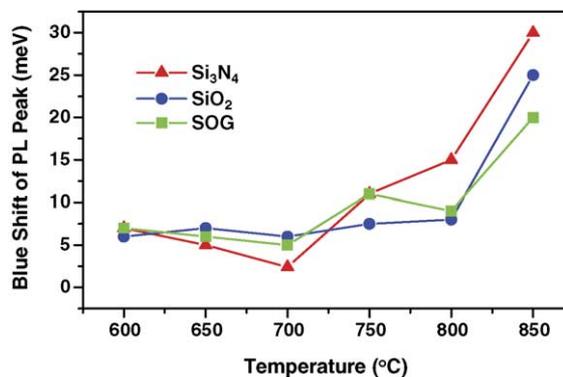


Fig. 3. The temperature dependence of blue shift for different dielectric covered samples.

The quantum well intermixing by IFVD can also be proved by high resolution SIMS profile measurement. Fig. 4 shows the SIMS profile of Ga and As ions from the control sample and the sample annealed at 800 °C, respectively. It can be clearly observed that Ga and As diffused out of the quantum well region, especially towards the inside of the bulk. The distribution of Ga and As in quantum well region becomes smooth compared with the control sample. The SIMS profile for the sample annealed at lower temperature (600–700 °C) is as close as the control sample, indicating there is no evident intermixing that happened at this temperature. It is consistent with the results of PL measurement above.

#### 3.2. SiO<sub>2</sub> and SOG covered samples

In comparison with Si<sub>3</sub>N<sub>4</sub> covered sample, the blue shifts of SiO<sub>2</sub> covered sample and SOG covered sample are smaller than the Si<sub>3</sub>N<sub>4</sub> one. At 800 °C, the blue shift of SiO<sub>2</sub> covered sample is 9 meV and the SOG covered sample is 10 meV, respectively (Fig. 2). Fig. 3 also shows the band gap blue shift versus the annealing temperature for the three kinds of samples, indicating that the combination of InP cladding layer and the Si<sub>3</sub>N<sub>4</sub> dielectric layer can create more intermixing which caused more blue shift.

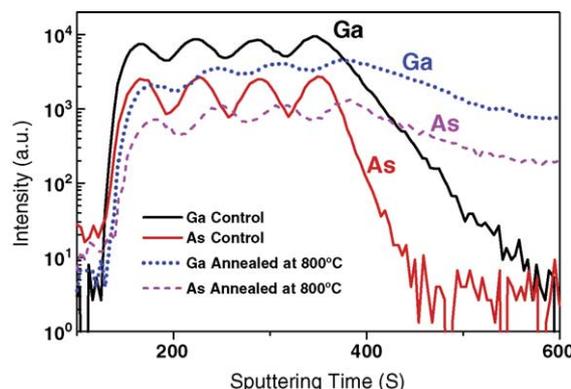


Fig. 4. SIMS characterization of control sample and sample treated by IFVD.

### 3.3. The effect on the combination between cladding layer and dielectric covered layer

In order to find the effects on the combination of cladding layer and dielectric covered layer, two cladding structure samples were performed in the PL measurement. One of them is the InP cladding structure, the other is the InGaAs cladding layer. All the structures for the MQWs are the same except for the top cladding layer. Keeping the same experimental condition for these two kinds of samples, the band gap blue shift caused by different dielectric covered layers of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  was measured. The results of band gap blue shifts can be observed that the blue shift of the combination of InP and  $\text{Si}_3\text{N}_4$  reached 30 meV at 850 °C; however, the blue shift for the combination of InP and  $\text{SiO}_2$  is only 25 meV. On the other hand, the combination of InGaAs with  $\text{SiO}_2$  covered layer creates 43 meV, but the combination of InGaAs with  $\text{Si}_3\text{N}_4$  covered layer can only reach 20 meV. Therefore, the combination of cladding layer and dielectric layer also affects the band gap tailing.

## 4. Conclusion

Summarizing the results of photoluminescence and SIMS characterization above for the three kinds of samples, the following conclusion can be drawn:

1. The band gap of quantum well structure of InGaAs/InP can be tailed by IFVD at certain conditions.
2. The blue shift of the band gap of InGaAs/InP structure depends on the dielectric layers, such as  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ , SOG, and annealing condition.
3. The blue shift of the band gap of InGaAs/InP structure also depends on the combination between cladding layer and dielectric layer.
4. The biggest blue shift of 30 meV can be reached with the combination of InP cladding layer and  $\text{Si}_3\text{N}_4$  dielectric covered layer annealed at 800 °C for 10 s.

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## References

- [1] W.K. Choi, Appl. Phys. Lett. 86 (2005) 021108.
- [2] D.G. Kim, Appl. Phys. Lett. 86 (2005) 021108.
- [3] H.S. Lim, IEEE Photonics Technol. Lett. 14 (2002) 594.
- [4] S. Kakimoto, J. Appl. Phys. 92 (2002) 6403.
- [5] K.S. Kim, Semicond. Sci. Technol. 15 (2000) 1005.
- [6] J. Zhao, Y.C. Wang, Surf. Coat. Technol. 131 (2000) 340.
- [7] H.-S. Kim, J.W. Park, D.K. Oh, K.R. Oh, S.J. Kim, I.-H. Choi, Semicond. Sci. Technol. 15 (2000) 1005.
- [8] D. Hofstetter, B. Maisenhölder, H.P. Zappe, IEEE J. Sel. Top. Quantum Electron. 4 (1998) 794.
- [9] J.H. Marsh, Semicond. Sci. Technol. 8 (1993) 1136.
- [10] D. Gdeepe, N. Holonyak Jr., J. Appl. Phys. 64 (1988) R93.
- [11] P.G. Piva, R.D. Goldberg, I.V. Mitchell, H. Chen, R.M. Feenstra, G.C. Weatherly, D.W. McComb, G.C. Aers, P.J. Poole, S. Charbonneau, Appl. Phys. Lett. 72 (1998) 1599.
- [12] S.R. Andrew, J.H. Marsh, M.C. Holland, A.H. Kean, IEEE Photonics Technol. Lett. 4 (1992) 426.
- [13] B.B. Elenkrig, D.A. Thompson, J.G. Simmons, D.M. Bruce, Yu. Si, Jie Zhao, J.D. Evans, I.M. Templeton, Appl. Phys. Lett. 65 (1994) 1239.
- [14] M. Paquette, J. Beauvais, J. Beerens, P.J. Poole, S. Charbonneau, C.J. Miner, C. Blaauw, Appl. Phys. Lett. 71 (1997) 3749.
- [15] J.H. Lee, S.K. Si, Y.B. Moon, E.J. Yoon, S.J. Kim, Electron. Lett. 33 (1997) 1179.
- [16] G. Li, S.J. Chua, S.J. Xu, X.C. Wang, A. Saher Helmy, Mao-Long, Ke, J.H. Marsh, Appl. Phys. Lett. 73 (1998) 3393.
- [17] J.S. Yu, J.D. Song, Y.T. Lee, J. Appl. Phys. 92 (2002) 1386.
- [18] S. O'Brien, J.R. Shealy, D.P. Bour, L. Elbaum, J.Y. Chi, Appl. Phys. Lett. 56 (1990) 1365.
- [19] S. Burkner, M. Maier, E.C. Larkins, W. Rothmund, E.P. O'Reilly, J.D. Ralston, J. Electron. Mater. 24 (1995) 805.
- [20] G. Li, S.J. Chua, J.H. Teng, W. Wang, Z.C. Feng, H. Huang, T. Osipowicz, J. Vac. Sci. Technol., B 17 (1999) 1507.
- [21] J.H. Teng, J.R. Dong, S.J. Chua, D.A. Thompson, B.J. Robinson, A.S.W. Lee, J. Hazell, I. Sproule, Mater. Sci. Semicond. Process. 4 (2001) 621.
- [22] F. Camacho, E.A. Avrutin, P. Cusumano, A.S. Helmy, A.C. Bryce, J.H. Marsh, IEEE Photonics Technol. Lett. 9 (1997) 1208.
- [23] W.J. Choi, S.M. Han, S.I. Shah, S.G. Choi, D.H. Woo, S. Lee, S.H. Kim, J.I. Lee, K.N. Kang, J. Cho, IEEE J. Sel. Top. Quantum Electron. 4 (1998) 624.
- [24] N. Shimada, Y. Fukumoto, M. Uemukai, T. Suhara, H. Nishihara, A. Larsson, Jpn. J. Appl. Phys. 39 (Part 1) (2000) 5914.