# A Large Bandgap Shift in InGaAs(P)/InP Multi-Quantum Well Structure Obtained by Impurity-Free Vacancy Diffusion Using $SiO_2$ Capping and Its Application to Photodetectors

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## ABSTRACT

In this paper, we have investigated the bandgap tuning in the InGaAs (P)/ InP multiquantum well (MQW) structure obtained by impurity-free vacancy diffusion (IFVD) using low temperature photoluminescence (PL). The MQW intermixing was performed in a rapid thermal annealer (RTA) using the dielectric capping materials, $SiO_2$ and $SiN_x$. The $SiO_2$ capping was successfully used with InGaAs cap layer to cause a large bandgap tuning effect in the InGaAs/InP MQW material. The blue shift of bandgap energy after RTA treatment was as much as 185 and 230 meV at 750℃ and 850 ℃, respectively, with its value controllable using annealing time and temperature. Samples with $SiO_2$-InP or $SiN_x$-InGaAs cap layer combinations, on the other hand, did not show any significant energy shifts. The absorption spectra taken from the same samples confimed the energy shifts obtained using PL. The process developed can be readily applied to fabrication of photodetectors that are sensitive to wavelength and/or polarization.

**Key words**: InGaAs/InP multi quantum wells (MQW's), Optoelectronic devices, Bandgap tuning, Impurity - free vacancy diffusion (IFVD), Impurity-induced disordering (IID), Quantum well intermixing, Self-interdiffusion, Absorption, Photodetectors, Demultiplexer, Wavelength-Selective, Polarization-Selective.

## 1. INTRODUCTION

The bandgap tuning of multiquantum well (MQW) structures in the compound semiconductors is becoming an important tool in optoelectronic or photonic integration [1]. To integrate several optoelectronic devices on a single wafer, we must divide the area with different optoelectronic properties such as absorption wavelength, refractive index, and material resistivity. A regrowth technique can be used for this purpose, but is expensive and complicated. Spatial bandgap tuning through the quantum confined Stark effect can also be used, but the degree of bandgap shift and refractive index change is quite limited [2].

There are several quantum well (QW) intermixing techniques available that provide the localized formation of bandgap shifted areas. Among them, impurity induced disordering (IID) and impurity-free vacancy diffusion (IFVD) have been extensively studied in recent years. In the IID technique [3], shallow dopants, such as Zn or Si, are used which are known to enhance the interdiffusion of Al and Ga or As and P atoms, causing intermixing of the structure of QW. The diffusing dopants can be either n or p type and may occupy either group III or V lattice sites. However, the impurities cause free carrier absorption and propagation loss in waveguides. In contrast, no impurities need to be introduced in an IFVD process, therefore the latter has been the favored choice in recent years [4,5].

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Typically, an IFVD method involves thermal annealing using a dielectric capping material. $SiO_2$ is known to induce an out-diffusion of Ga during annealing and generate vacancies in GaAs [6]. This way, a GaAs/AlGaAs QW structure, when annealed using RTA with $SiO_2$ capping would show a large blue shift in their photoluminescence (PL) characteristics [7]. The vacancies generated at the group III sublattice diffuse to the barriers and promote the diffusion Al into the QW. This in turn raises the bandgap and effectively narrows the well width.

In the GaAs/AlGaAs QW, the intermixing can be produced using $SiO_2$ capping [4], while the use of $SiN_x$ layer did not show any bandgap shift [1]. On the other hand, in the InGaAs / InP QW system, the intermixing was demonstrated using $SiN_x$ capping [8]. The details on this discrepancy has not been shown. In this paper, we report the large bandgap tuning of an InGaAs/InP MQW structure using $SiO_2$ capping. We also compare experimentally the use of dielectric capping layers ($SiO_2$ and $SiN_x$) and semiconductor cap layers (InP and InGaAs). The result shownin this work would indicate the mechanisms of intermixing in this material system. In addition to the characterization using photoluminescence (PL), the absorption spectra of intermixed MQWs are also shown. This technology can be easily applied to various devices including photodetectors and semiconductor amplifiers. A waveguide photodetector structure is proposed that can differentiate wavelength and polarization of incoming light.

## 2. EXPERIMENTAL

Two structures of MQW (hereafter called as structure A and B) were grown by low pressure metal organic chemical vapor deposition (MOCVD). Structure A was grown on an n-type ($1 \times 10^{18} cm^{-3}$) InP substrate and consisted of 30 pairs of 50 Å undoped InGaAs wells and 100 Å undoped InP barriers. A 0.5 $\mu m$ p-type ($5 \times 10^{17} cm^{-3}$) InP clad layer was then grown followed by the deposition of a 0.1 $\mu m$ $p^+$-type ($1 \times 10^{19} cm^{-3}$) InGaAs cap layer. The structure is schematically shown in Fig. 1. The epitaxial structure of B was similar to that of A except that the InGaAs wells were replaced with InGaAsP wells of 10 pairs with 45 Å thickness. For p-type and n-type dopants, Zn and Si were used, respectively. One important aspect of our work is that we used InGaAs cap layer instead of InP.

A 1500-1700 Å thick $SiO_2$ layer was deposited on the epitaixal samples using atmospheric pressure chemical vapor deposition (AP-CVD) at 250℃ and samples were cleaved into small pieces (~ 4 x 4 $mm^2$). Then, samples were mounted face down in close contact with a freshly polished Sn-doped InP substrate for an annealing. Rapid thermal annealing (RTA) was performed under an $N_2$ flux for 40s at various anneal temperatures. For comparison, a 1500-1700 Å thick $SiN_x$ layer was also deposited in other samples by plasma enhanced chemical vapor deposition (PECVD) at 300℃.

Low temperature PL measurements were made at 10K using a closed He refrigerator. The samples were excited with the 632.8 nm line from He-Ne laser. Luminescence was dispersed using a 0.5 m monochromator at a spectral resolution of 0.5 nm and detected by liquid nitrogen cooled Ge detector. The absorption spectra of the intermixed MQW were measured using a white light source and a monochormator. The light was irradiated on the sample and the transmission was monitored using the monochromator. The intensity was adjusted so as to avoid the nonlinear effects that can occur at excessive light power density.

## 3. RESULTS AND DISCUSSION

Fig.2 shows the normalized PL spectra of the as-grown sample and the samples treated with IFVD. The samples with $SiO_2$-InGaAs cap layers were RTA annealed for 40s at various temperatures. The bandgap energy of the as-grown sample is 0.898 eV at 10K, which matches well with the calculated value for 50 Å InGaAs well width. For IFVD treated samples, the bandgap energy shifts to a higher energy and the amount of blue shift depends on the RTA temperature. The energy shifts are 53, 91, 185, and 230 meV for annealing temperatures of 650℃, 700℃, 750℃, and 850℃, respectively for an annealing time of 40 seconds.

In other samples, we deposited $SiO_2$ capping layer directly on the InP clad layer without the InGaAs cap layer. Using the identical epitaxial structure, we have removed the InGaAs cap layer by selective wet etching of $H_3PO_4$: $H_2O_2$: $5H_2O$ solution. It is noted that the bandgap shift in this case is negligible up to 750 ℃. We also tried $SiN_x$ capping on the InGaAs cap layer, but no significant bandgap blue shifts were observed in this case either. Instead, the bandgap actually is seen to show a slight shift towards lower energy. The amount of red-shift (shift to lower energy) is -4, -8 and -27 meV for annealing temperatures of 650℃, 700℃ and 750℃, respectively. In another experiment, InGaAs cap layer was tried on the InP clad layer without InGaAs cap. In this case again, there was no bandgap shift for the RTA temperatures up to 750 ℃. The above results are summarized in Fig. 3 where the amount of blue or red energy shifts are displayed as a function of RTA anneal temperature.

Clearly the simultaneous use of $SiO_2$ capping and the InGaAs cap layer was important in causing significant and usable blue shifts. Other combinations did not produce any blue shifts or a slight red shift in one case. We offer following explanations for these experimental results. First on the combination of $SiO_2$ and InGaAs cap material produce the largest amount of vacancies at the interface. The vacancies are produced in both group III and V. It is known in GaAs materials that the following reactions are prompted to produce large amount of Ga vacancies at the interface.

$$\begin{aligned} &4GaAs + 3SiO_2 \Leftrightarrow 4Ga + 2As_2O_3 + 3Si \\ &As_2O_3 + 2GaAs \Leftrightarrow Ga_2O_3 + 4As \end{aligned} \qquad (1)$$

As for the group V vacancies, we can not provide the detailed reactions as to how the vacancies are produced at this structure. However, our results indicate that there have to be at least equal number of group V (As or P) vacancies produced to cause such a large blue shift. For the other three combinations of dielectric-cap layers, the amount of vacancies generated are significantly less than in the $SiO_2$-InGaAs pair. Absence of Ga can explain such reduction of vacancies in the $SiO_2$-InP case. In the case of $SiN_x$-InGaAs pair, the dense and void-free nature of the dielectric may have reduced the vacancies.

The small red shift found in this case was reproducible and may indicate that the generation of group V vacancies were slightly more active than the group III counterparts. The latter tend to enhance the IID effect of the Zn diffusion [3]. As we have explained earlier, our epitaxial structure included Zn doped clad layers on top of the MQW region. This IID effect caused by Zn would show red shift in this material system. When there is no dielectric capping, the shifts were negligible and no red shifts were displayed for the temperature range used. We have not tried higher temperatures than 750 ℃ for the last three cases, but we expect the samples would show some blue shifts due to self-intermixing at those high temperatures [9]. In the temperatures less than 750 ℃, we think that the two effects, the red (IID) and the blue (Self-mixing) shift effects, co-exist and balance each other. The $SiO_2$-InGaAs combination has been previously used [10] in InGaAs/ InGaAlAs quantum well material system. In this case, however, there are only group III diffusing elements. In our case, group V elements have to diffuse to cause the blue energy shifts that were observed.

The same technique has been applied to the InGaAsP/InP MQW materials (structure B). As indicated earlier, this structure included InGaAsP wells of 10 periods instead of InGaAs wells. The bandgap energy of the as-grown sample was 0.93 eV (1.34 ㎛) at 10K. Fig.4 shows the PL characteristics of this material after the RTA processing of the samples where the $SiO_2$-InGaAs combination was used. The maximum energy shift found for this material was 170 meV at the RTA temperature of 850 ℃ for 30 s. Also shown in the figure is the data for the sample where no dielectric capping was applied. Again some red shift is observed in the latter.

Absorption spectrum has been measured from structure B. Fig. 5 (a) and (b) show the measured absorption spectra of intermixed MQW's, taken at both room temperature and liquid nitrogen temperature (77K), respectively. The spectral responses of intermixed MQWs show blue shifts and the amount of blue shifts increases as the RTA time, as the PL data indicated. We notice some bandgap narrowing at room temperature absorption compared to the absorption at 77 K. In terms of showing blue shift trends, the two figures are similar. The amount of blue shifts match closely to those obtained from the PL data previously described.

The technology described above can be applied to devices useful in wavelength division multiplexing (WDM) applications. As an example, Fig. 6 shows a wavelength demultiplexer. The incoming light is incident on the waveguide device where the intermixing processing has been applied so the bandgap is wider for the first segment, but is narrower for the second. We can design it in such a way that a light with shorter wavelength is absorbed by the first segment, but one with longer wavelength is transparent. Thus the the device with two segments of different bandgap can be used for wavelength detection. The same structure can be used to detect polarization due to the polarization dependence of absorption of the quantum wells where the subband energies are made to shift by the intermixing technique mentioned above.

## 4. CONCLUSION

In conclusion, we have investigated the bandgap tuning of InGaAs(P)/InP MQW structure using an IFVD method. We have shown that the simultaneous use of $SiO_2$ capping and InGaAs cap layer was critical. Large bandgap blue shifts results and the amount of bandgap energy shift could be controlled by selection of thermal annealing temperature and time. The maximum amount of bandgap energy shift was 230 meV for an RTA annealing temperature of 850 ℃. Samples with $SiO_2$-InP or $SiN_x$-InGaAs cap layer combinations did not show significant energy shift. The bandgap shift data were confirmed in the absorption spectra measured from the intermixed InGaAsP/InP MQW materials. This technology is simple to apply and cost-effective, so that we believe fabrication of many WDM related devices can benefit from it.

## 5. ACKNOWLEDGMENT

This work was financially supported in part by OERC(Opto-Electronic Research Center) through the grant # 97K3-0809-02-06-1 and by the SPRC (Semiconductor Physics Research Center) of Korea. The authors thank U. H. Lee and Prof. D. Lee of Chung Nam National Univ. for their help with the absorption measurement.

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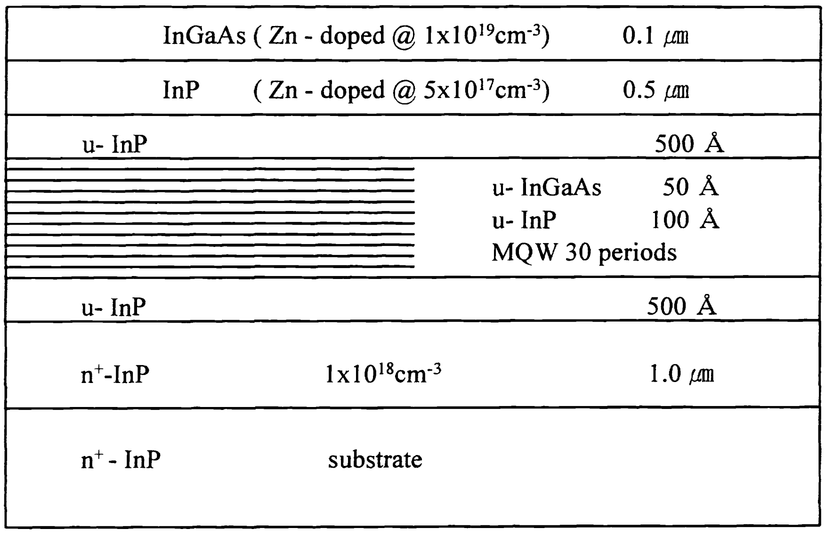


Fig. 1 Schematic cross-sectional view of the MQW structure

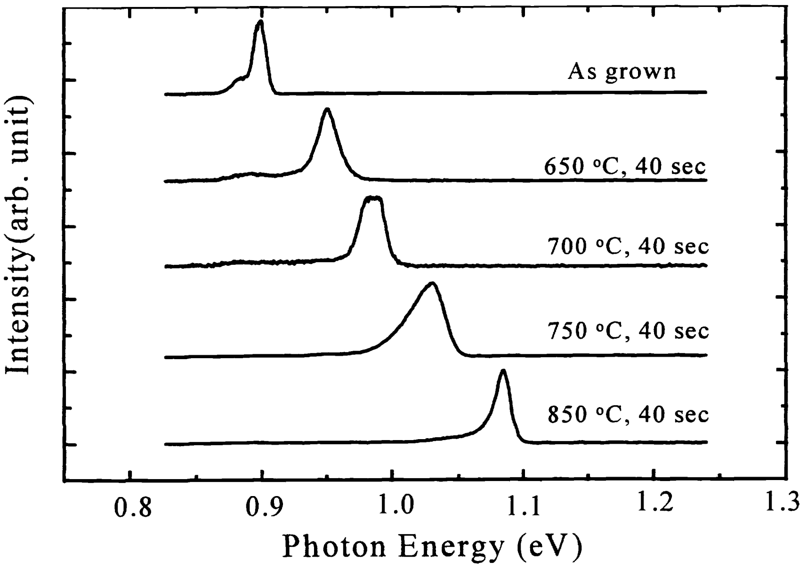


Fig. 2. Normalized photoluminescence (PL) spectra obtained when $SiO_2$ capping was used on top of structure in Fig. 1 during RTA annealing for 40s at various temperatures (a) As-grown (b) 650℃, 40s (c) 700℃, 40s (d) 750℃, 40s (e) 850℃, 40s

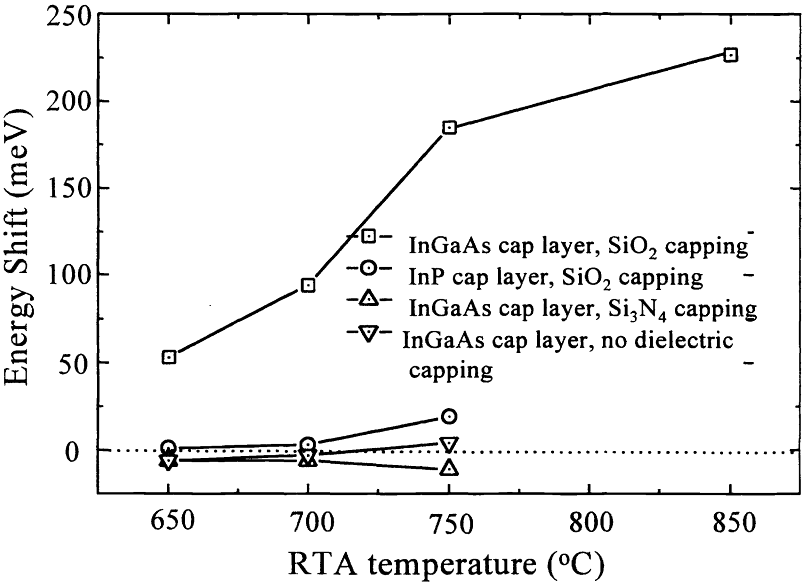


Fig.3. Photoluminescence (PL) peak energy shifts of MQW samples with $SiO_2$ capping on InGaAs cap layer, $SiO_2$ capping on InP cap layer, SiNx capping on InGaAs cap layer, and InGaAs cap layer and no dielectric capping, annealed at various RTA temperatures for 40s.

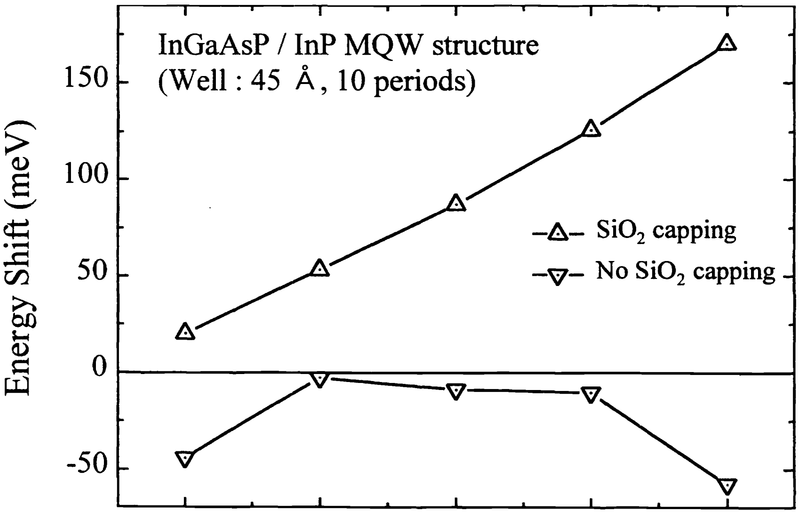
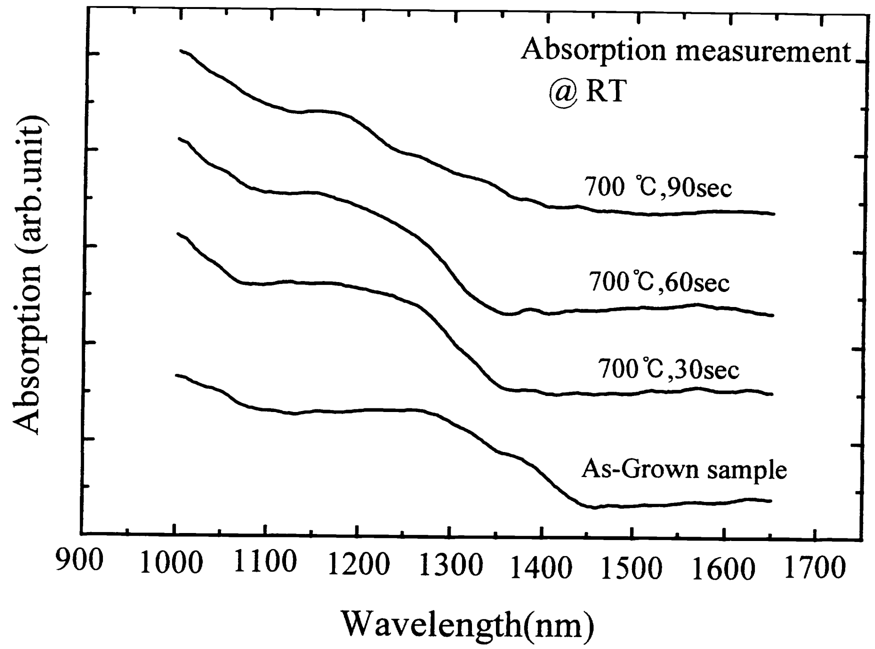
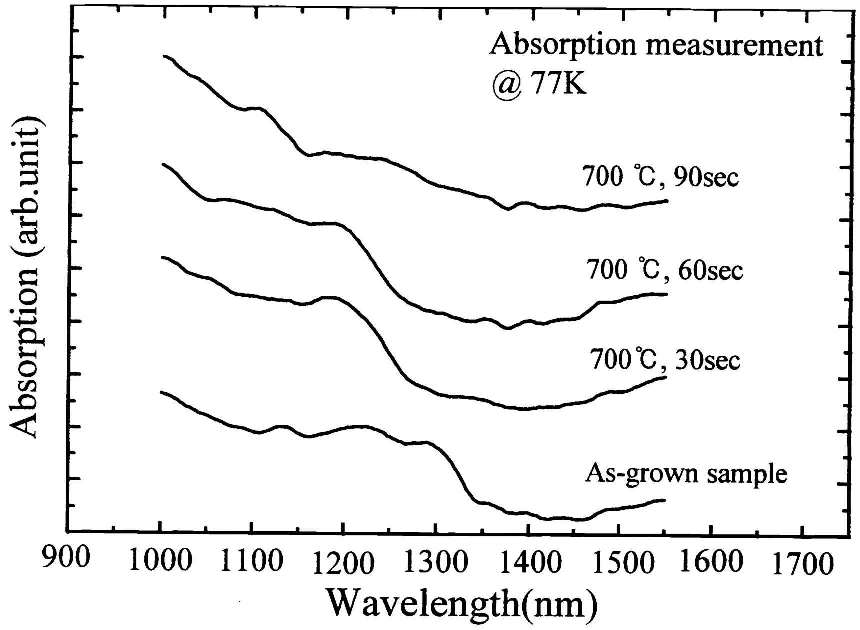


Fig. 4 PL peak energy shifts as a function of the annealing temperature for the InGaAsP/InP MQW structure capped with and without $SiO_2$ annealed at various RTA temperatures for 30 s.



(a)



(b)

Fig.5. Absorption spectra of intermixed InGaAsP/InP MQW structure (a) room temperature (b) liquid nitrogen temperature (77K).

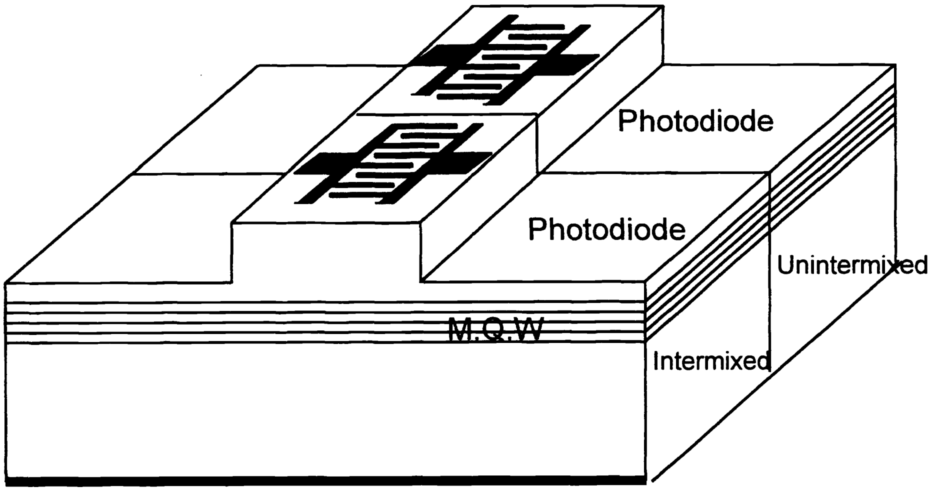


Fig. 6 Schematic diagram of waveguide type demultiplexing photodiode