Influence of SiO_2 and TiO_2 dielectric layers on the atomic intermixing of $In_xGa_{1-x}As$/InP quantum well structures

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Abstract

We have studied the influence of SiO_2 and TiO_2 dielectric layers on the atomic intermixing of $In_xGa_{1-x}As$/InP quantum well structures using the impurity-free vacancy disordering technique. Photoluminescence results revealed that an enhancement of interdiffusion was obtained when the samples were capped with SiO_2. Although TiO_2 layers were able to suppress the interdiffusion in the InGaAs/InP system, the suppression was not significant compared to the AlGaAs/GaAs system. Based on a fitting procedure that was deconvoluted from the photoluminescence spectra as well as a theoretical modeling, the electron–heavy hole and electron–light hole transitions were identified, and a ratio of the group V to the group III diffusion coefficients (k) was obtained. The k ratio of the InGaAs/InP samples capped with SiO_2 is relatively larger than that of samples capped with TiO_2 layers.

1. Introduction

Quantum well intermixing or interdiffusion (QWI) is a post-growth method that enables the monolithic integration of different optoelectronic devices to be achieved. This method selectively modifies the bandgap of quantum well structures by intermixing the group V and group III atoms of the quantum well and barrier regions [1, 2]. There are several approaches for QWI, such as impurity induced ordering [3], impurity-free vacancy disordering (IFVD) [4, 5] and ion irradiation induced intermixing [6–8]. Among these various techniques, intermixing by impurity free vacancy disordering (IFVD) has shown to be effective for device applications since it is simple and the amount of residual defects that are created by the interdiffusion process is much lower than ion implantation and impurity diffusion. There have been numerous reports of IFVD techniques in the AlGaAs/GaAs or the AlGaAs/InGaAs system [9–11]. However, that is very different from the InGaAs/InP system that will be presented in this study. Intermixing of the InGaAs/InP system has an added degree of complexity, since there is the possibility of both group III

and group V interdiffusion across the InP/InGaAs interface [12, 13], unlike the InGaAs/AlGaAs quantum well system where only group III interdiffusion needs to be taken into account. Previous studies of InGaAs/InP interdiffusion using a range of techniques such as ion implantation induced intermixing and IFVD have reported varying ratios between group III and group V diffusion rates [14–16]. As a result of the differences between group III and group V diffusion coefficients, a lattice-matched InGaAs/InP QW structure for example will no longer remain to be lattice-matched after interdiffusion and thus strain will be introduced into the system.

In the IFVD technique, defects caused by the presence of dielectric layers (such as SiO_2) on the surface of the samples move across to the quantum well region during annealing, and thereby causing interdiffusion [11]. Considering an AlGaAs/GaAs structure with a top surface capped with SiO_2, Ga will outdiffuse from the GaAs surface into the dielectric layer during annealing resulting in the production of group III vacancies at the interface, which diffuse into the sample. This diffusion of Ga vacancies enhances the interdiffusion
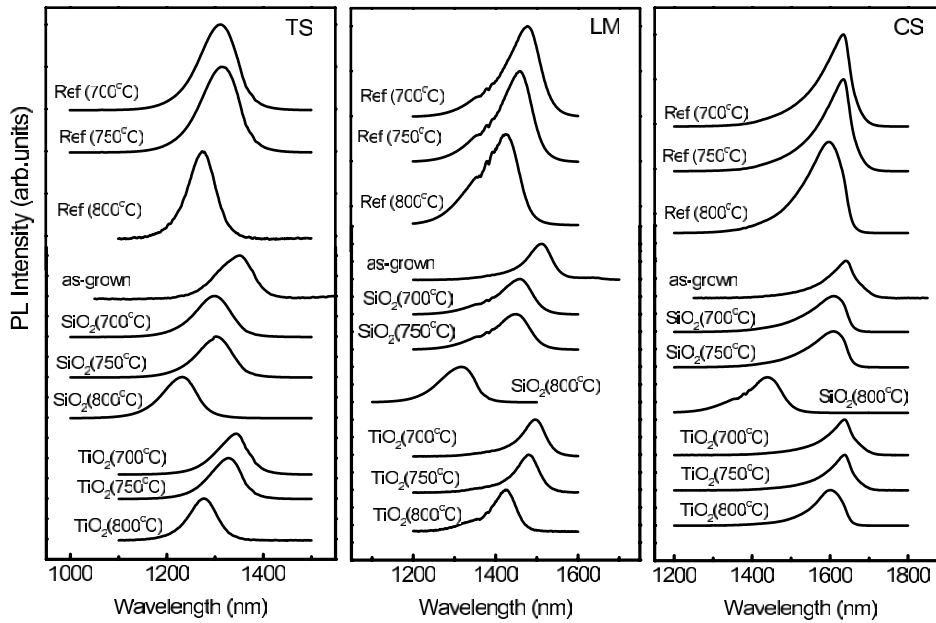
Figure 1. Photoluminescence (PL) spectra of tensile-strained (TS), lattice-matched (LM) and compressively-strained (CS) In$_x$Ga$_{1-x}$As/InP QWs capping with SiO$_2$ and TiO$_2$ layers after annealing with various temperatures from 700 °C to 800 °C. The PL spectra from as-grown and annealed samples without capping layers are also shown for comparison. Spectra are vertically shifted for clarity.

of atoms between the barrier and quantum well [17, 18]. Similar to this system, in the InGaAs/InP system, an InGaAs capping layer was employed between the dielectric layer and the top InP barrier layer to enhance the interdiffusion. For device integration, it is also important to have a capping layer that protects regions where the interdiffusion is not desired. Previous studies have reported that TiO$_2$ dielectric layers are able to provide some suppression of the intermixing in the InGaAs/AlGaAs system [10]. In this present study, we investigate the influence of SiO$_2$ and TiO$_2$ dielectric layers on the atomic intermixing of In$_x$Ga$_{1-x}$As/InP QWs.

2. Experimental details

Three different indium compositions of In$_x$Ga$_{1-x}$As QWs, lattice-matched (LM, $x = 0.53$), compressively-strained (CS, $x = 0.68$) and tensile-strained (TS, $x = 0.38$) were grown on (1 0 0) semi-insulating InP substrates by low pressure metalorganic chemical vapor deposition (MOCVD) at a growth temperature of 650 °C. Each of samples consisted of a 600 nm InP buffer layer, a 5 nm In$_x$Ga$_{1-x}$As QW, a 200 nm InP layer followed by a 100 nm In$_{0.53}$Ga$_{0.47}$As capping layer. Dielectric layers of either SiO$_2$ or TiO$_2$ were deposited on the top layer of the samples. Silicon dioxide with a thickness of 200 nm was deposited by plasma-enhanced chemical vapor deposition (PECVD) using a N$_2$O/SiH$_4$ mixture at room temperature. On each half of the samples, SiO$_2$ layers were etched off by 10% HF after deposition to provide a dielectric-free reference region. TiO$_2$ layers with a nominal thickness of 200 nm were deposited by electron beam evaporation. In order to create the reference regions, half of each sample was covered with a mask prior to the TiO$_2$ deposition. All the samples were annealed under Ar flow in a rapid thermal annealer in the temperature range of 700–850 °C for 60 s. During the annealing process the samples were sandwiched

between fresh InP and/or GaAs substrates to minimize the evaporation of P and As atoms from the surface of the samples. For samples with the top InGaAs layer, this layer was removed (etched) after annealing to improve the intensity of the PL spectra since this layer absorbed the emission from the QW. Room temperature photoluminescence (PL) measurements were performed to characterize the energy shift of the emission from the QW. The shift of the PL peak between the dielectric coated side and the reference (uncoated side) region was then calculated.

3. Results and discussion

Figure 1 shows graphs of the PL spectra of the TS, LM and CS QWs that were annealed with or without SiO$_2$ and TiO$_2$ dielectric layers. Also, it shows the PL spectra of TS, LM, CS as-grown samples for comparison. For the samples capped with SiO$_2$, a small blueshift was observed for LM, TS and CS QWs after annealing at 700 °C and 750 °C. Annealing these samples at 800 °C resulted in a more significant shift compared with the as-grown samples. In contrast, for TiO$_2$ capped samples, hardly any shift was observed in the PL peak after annealing at either 700 °C or 750 °C compared with as-grown samples. A smaller but noticeable blueshift in wavelength was clearly observed when the samples were annealed at 800 °C.

A plot of energy shift of the LM, CS and TS QWs as a function of annealing temperature with and without SiO$_2$ and TiO$_2$ dielectric layers are shown in figure 2. In addition, the energy shift of samples annealed without any dielectric cap is also plotted for comparison. As can be seen from this figure, the thermal component of diffusion becomes only significant above 750 °C. At 850 °C, this effect was about 100 meV for all the three samples. The SiO$_2$ capped samples also did not show any significant energy shift up to 750 °C. Beyond
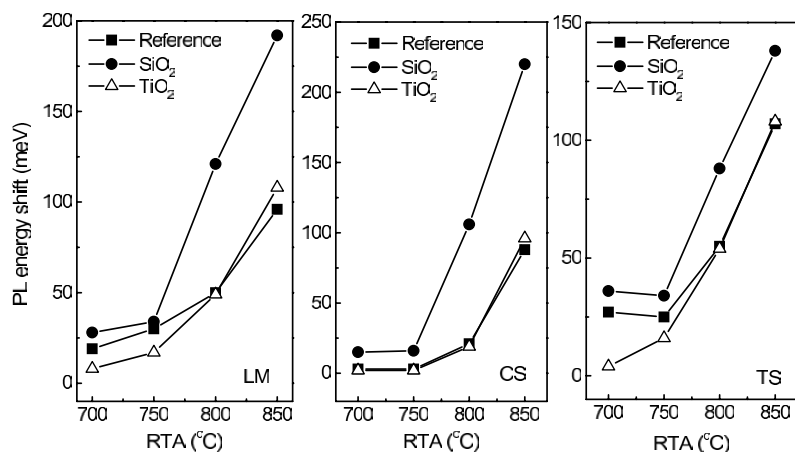
Figure 2. The PL energy shift of lattice-matched (LM), compressively-strained (CS), and tensile-strained (TS) In$_x$Ga$_{1-x}$As/InP QWs with and without SiO$_2$ and TiO$_2$ layers as a function of annealing temperature.

this annealing temperature, there was a marked increase of energy shift, in addition to the thermal component. At 850 °C, the additional energy shift caused by the SiO$_2$ layer was about 100, 130 and 30 meV for the LM, CS and TS QW, respectively. The As–P concentration gradient across the QW is the same in all three samples but the In–Ga concentration gradient is the highest for the TS QW, followed by the LM and CS QWs. Assuming a constant group V diffusion (which gives a blueshift), the smaller energy shift observed for the TS QW could be due to the higher group III diffusion rate since this QW has the highest concentration In–Ga gradient. Hence the redshift induced by group III diffusion may counter the effect of the group V diffusion. Similarly, this argument could be applied to the other two types of QWs. However, this effect has to be related to the strain induced by the SiO$_2$ layer during annealing since the thermal diffusion component is the same in all three QWs. It is also possible that the diffusion of In into the CS and LM QW increased the strain of the QW which then in turn provided a driving force for P diffusion into the QW to negate the strain. In the case of TS QW, the already tensile strain in the QW decreases the affinity for the P diffusion into the QW and hence less blueshift. Group III and group V interdiffusions in this material system are intrinsically convoluted to each other and become further complicated by the effect of strain.

In the case of TiO$_2$, the trends for all three types of QWs are very similar to those of the reference. It has been reported in the previous studies, TiO$_2$ is able to provide some suppression to intermixing. In the case of the InGaAs/InP system, only very small suppression can be seen in figure 2 for the LM and TS QWs up to 750 °C. Above this temperature, the suppression becomes ineffective against the thermal diffusion. For the CS QW, the TiO$_2$ layer did not provide any suppression at all in the temperature range investigated.

A theoretical modeling of the interdiffusion was performed to obtain further insight of the interdiffusion and strain issues in this material system with an assumption that both group-V and group-III sublattices were Fickian for all the samples during the interdiffusion. Two independent coefficients D$_{III}$ and D$_V$, characterizing the isotropic interdiffusion of group III and group V constituent elements were used, respectively. The factor k is defined
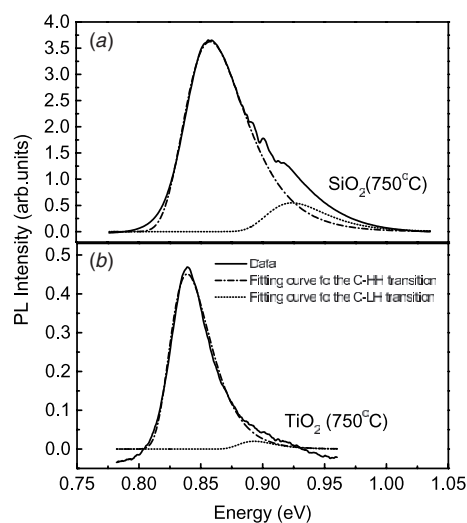

Figure 3. The photoluminescence spectra of InGaAs/InP lattice-matched QWs after annealing at 750 °C for 60 s capping with SiO$_2$ and TiO$_2$. An experimental spectrum was fitted with two Gaussian curves as shown by the broken lines.

as the ratio L$_V$/L$_{III}$ are diffusion lengths corresponding to the two sub-lattices: L$_{III,V}$ = $2\sqrt{D_{III,V}t}$. The diffusion coefficients are assumed to be independent of the concentration of the diffusing element. The error function is used to simulate the interdiffusion at hetero-interfaces by creating a more parabolic-type profile instead of sharp step. From the composition profiles, the valence and conduction band profiles are calculated and corresponding Schrödinger equations are solved using a transfer matrix method to provide the energies of the photoluminescence transitions. The layers are assumed to be fully strained and the material constants corresponding to each composition are taken from [19]. The model does not include calculation of the shift in transition energy due to excitonic binding energies or quantum-confined Stark effects.

The compositional profile from this model was used to calculate the electron–heavy-hole (C–HH) and the electron–light-hole (C–LH) transition energy. From the asymmetrical PL peaks, the electron–heavy hole (C–HH) and electron–light hole (C–LH) were first deconvoluted using fitting procedures.
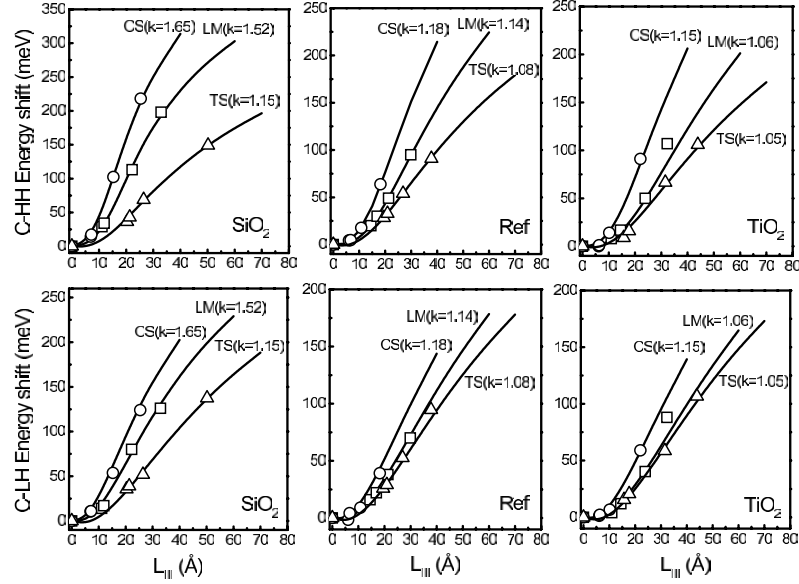
Figure 4. Transitions energy of C–HH and C–LH as a function of diffusion length in the group III sublattices with the ratio k $=$ L$_V$/L$_{III}$ as a variable parameter. The lines represent modeled results, the triangles, squares and circles represent experimental results.

One such example is shown in figure 3(a) for the LM QW capped with SiO$_2$ and annealed at 750 °C. Fitting this spectrum with two Gaussian profiles resulted in the C–HH transition at 0.856 eV and the C–LH transition at 0.898 eV. Similarly, in the case of TiO$_2$ annealed at 750 °C, C–HH transition was at 0.839 eV and the C–LH at 0.893 eV, as shown in figure 3(b). The model was then used to determine the unique value of k ratio that fit both these (C–HH and C–LH) transitions as plotted in figure 4 for the SiO$_2$ capped, TiO$_2$ capped and reference QWs.

The k ratio for the TS and LM and CS samples capped with SiO$_2$ was determined to be 1.15, 1.52 and 1.65, respectively. These values were higher than unity indicating that the diffusion coefficient of the group V sublattice was larger than the diffusion coefficient of the group III sublattice atoms. For the TiO$_2$ case, the k ratio for TS, LM and CS was 1.05, 1.06 and 1.15, respectively. These values were similar to those obtained for the reference samples. It is also worth noting that in all cases the k ratio is the largest in CS QW followed by LM and the smallest in TS QW.

Based on the results above, SiO$_2$ and TiO$_2$ are clearly seen to affect the degree of intermixing of In$_x$Ga$_{1-x}$As/InP QWs in different ways. The group V sublattice is more preferable to promote intermixing when the samples are covered with SiO$_2$ layers. In the case of TiO$_2$ capped samples, however, the group V sublattice is comparable to the group III sublattice. This indicates that both group V and group III sublattices would compete to promote intermixing. Our results here are further confirmed in previous studies [12]. Such work indicated that group III interdiffusion in InGaAs/InP is associated with a redshift, while a blueshift is associated with a dominant group V interdiffusion. To what extent the group V and group III interdiffusion contribute to the intermixing will be obtained by the ratio of the diffusion coefficients of the group V and the group III sublattices.

The k ratio obtained from this study (for SiO$_2$ capped samples) is larger than our previous study in ion implantation [16]. For example, in the LM case the k value is 1.52 by the IFVD method while for ion implantation it is 1.25. This is true for the three types of QWs. This indicates that the interdiffusion caused by IFVD and defect-assisted diffusion (ion implantation) are quite different. Most likely the outdiffusion of group III atoms into the SiO$_2$ layer is causing a stoichiometric imbalance on the surface and this destabilizing effect promotes the diffusion of group V atoms during the annealing step. The thermal stress imposed by the SiO$_2$ layer could also play a very important role in enhancing the diffusion of the group V atoms. Ion implantation on the other hand induced roughly an equal number of defects on both the group III and group V sublattices and thus they will intermix roughly equally [15]. Previous study on InGaAs/InP MQW structures has shown that the k ratio is about 1.7 if the implantation damage occurs in the cap layer (shallow implantation) [20], while for deep implantation (through the quantum well) the k ratio is around 0.8–0.9 [21].

4. Conclusion

The influence of SiO$_2$ and TiO$_2$ dielectric layers on the atomic interdiffusion of In$_x$Ga$_{1-x}$As/InP QWs has been studied. An enhancement of interdiffusion was obtained when the samples were capped with SiO$_2$ layers. In addition to this, the largest energy shift was observed in the CS QWs compared with LM and TS QWs after annealing at 850 °C. Very little suppression of thermally-induced interdiffusion was observed when the samples were capped with TiO$_2$, in contrast to the GaAs/AlGaAs system. In both cases, the k ratios were larger than unity indicating that the group V sublattice diffusion is still the more dominant effect, although for the TiO$_2$ case, these ratios were just slightly greater than unity. The k ratio in CS QW is the largest compared with two structures in all cases. This is due to the fact that the group III sublattice is smaller in the CS structure as a result of a smaller of indium gradient concentration from the barrier to the quantum well regions.

Acknowledgments

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