

Study of intermixing in a GaAs/AlGaAs quantum-well structure using doped spin-on silica layers

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The effect of two different dopants, P and Ga, in spin-on glass (SOG) films on impurity-free vacancy disordering (IFVD) in GaAs/AlGaAs quantum-well structures has been investigated. It is observed that by varying the annealing and baking temperatures, P-doped SOG films created a similar amount of intermixing as the undoped SOG films. This is different from the results of other studies of P-doped SiO₂ and is ascribed to the low doping concentration of P, indicating that the doping concentration of P in the SiO₂ layer is one of the key parameters that may control intermixing. On the other hand, for all the samples encapsulated with Ga-doped SOG layers, significant suppression of the intermixing was observed, making them very promising candidates with which to achieve the selective-area defect engineering that is required for any successful application of IFVD. © 2002 American Institute of Physics. [DOI: 10.1063/1.1449522]

For monolithic integration of optoelectronic devices, one of the primary requirements is the capability to selectively engineer the band gap of the semiconductor heterostructure across the wafer. To achieve this, the postgrowth technique, quantum-well intermixing (QWI),¹⁻³ has been found to be a useful and straightforward method. Among many techniques⁴⁻⁶ which have been used to create QWI, impurity free vacancy disordering (IFVD) has drawn great interest because it can retain high crystal quality while maintaining low optical propagation losses,^{7,8} as demonstrated by the successful fabrication of some photonic components such as low-loss optical waveguides, modulators, and quantum-well laser diodes.^{9,10} By simply depositing a layer of dielectric film (mostly SiO₂) on top of a quantum-well structure, followed by rapid thermal annealing (RTA), IFVD can be initiated. However, due to the wide variety of deposition techniques and processing parameters, the experimental results seem to not be reproducible, giving rise to concerns about the technological viability of IFVD. Recently, commercial spin-on glass (SOG) has been introduced to form the SiO₂ layer to promote IFVD.^{11,12} It is simple and inexpensive and is able to produce relatively stable film compositions with few process parameters. It has been demonstrated to create effective IFVD and also to show potential for monolithic integration of devices.^{11,12} In this work, SOG solutions doped with two different dopants, P and Ga, together with an undoped SOG solution were applied to the GaAs/AlGaAs QW structure. The P-doped SOG film was found to behave similarly to the undoped SOG in terms of promoting intermixing whereas a suppression effect was observed using Ga-doped SOG films.

The GaAs/AlGaAs structure used in this study was grown by metalorganic chemical vapor deposition

(MOCVD) on semi-insulating GaAs (100) substrates. From the surface, it contained two QWs with nominal thicknesses of 2.3 (QW1) and 4.0 nm (QW2), separated by 50 nm Al_{0.54}Ga_{0.46}As barriers. The structure was grown on top of a 1 μm GaAs buffer layer and terminated by a 40 nm GaAs capping layer. All layers were undoped and grown at 750 °C. Undoped, P-doped, and Ga-doped spin-on silica solutions were spun uniformly onto cleaved pieces of the QW structures at 3000 rpm for 30 s. The samples were then baked in a rapid thermal annealer in Ar flow at temperatures from 100 to 400 °C for 15 min and half of each sample was immersed into 10% HF to remove the oxide layer to provide an uncapped reference. Subsequent RTA at temperatures ranging from 800 to 925 °C for 60 s was also carried out in Ar flow and during annealing samples were sandwiched by two fresh pieces of GaAs to prevent desorption of As. Then, low temperature (12 K) photoluminescence (PL) was performed using a green He-Ne laser (543.5 nm) as the excitation source and the signal was detected by a silicon charge coupled device (CCD) through a 0.27 m monochromator.

The PL spectra obtained from the uncapped reference (solid line) and oxide capped (dashed line) parts of the samples with undoped, P-doped, and Ga-doped SOG films baked at 400 °C for 15 min and annealed at 875 °C for 60 s are shown in Fig. 1. Each spectrum shows two peaks which arise from the two QWs in the structure. Obviously, the samples capped with undoped and P-doped SOG layers exhibit larger wavelength blueshifts compared with the uncapped reference sample, whereas almost no blueshift can be observed for the sample covered with the Ga-doped SOG layer.

The differential PL energy shift between the reference region and the encapsulated region of the GaAs/AlGaAs samples as a function of the annealing temperature is displayed in Fig. 2. It shows that when the annealing temperature is below 825 °C, no significant intermixing occurs. At higher temperatures, the shifts in energy from the undoped and the P-doped SOG covered samples increase with the

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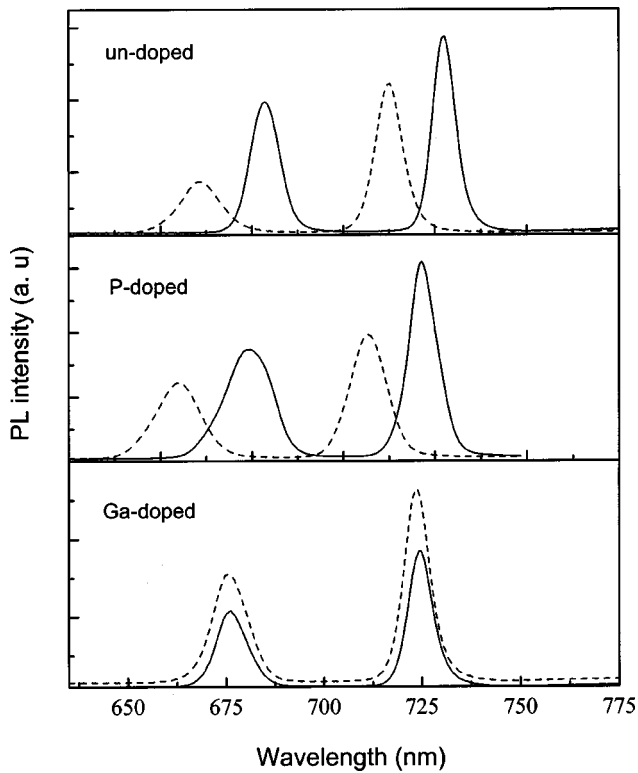


FIG. 1. PL spectra for the samples capped with undoped, P-doped, and Ga-doped SOG layers baked at 400 °C for 15 min and annealed at 875 °C for 60 s. PL spectra for the samples annealed under the same conditions but without a cap layer are also shown for reference (solid curves).

annealing temperature to a maximum value of ~200 meV. For each annealing temperature, a similar amount of intermixing was achieved by using the two films. For the case of Ga-doped SOG, under all the annealing temperatures, little blueshifting (<15 meV) is obtained, indicating that intermixing was suppressed. From the results in Fig. 2, the interdiffusion coefficient of Al across the GaAs/AlGaAs structure in the 4 nm thick QW2 was calculated and is plotted in the Fig. 3 as a function of the reciprocal of the annealing temperature, 1000/T, for undoped and P-doped encapsulants. From

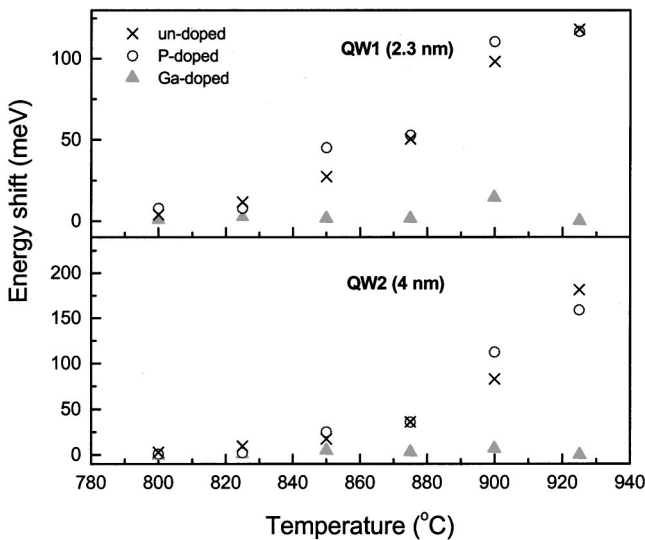


FIG. 2. PL energy blueshift obtained for the GaAs/AlGaAs samples after capping with 400 °C, 15 min baked undoped, P-doped, and Ga-doped SOG layers as a function of the annealing temperature.

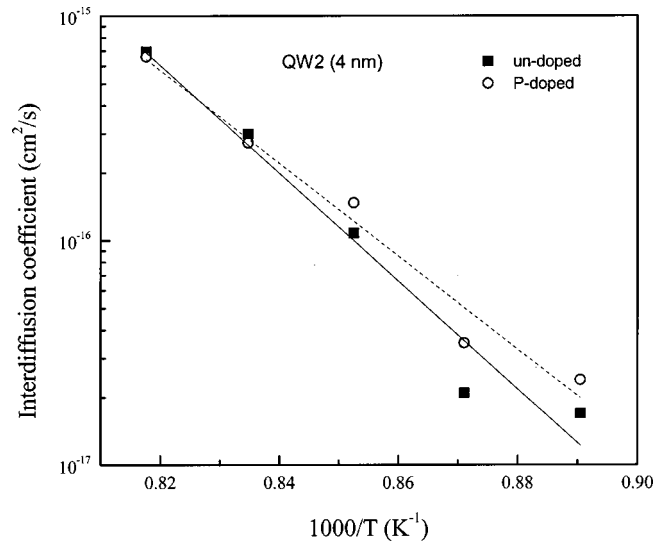


FIG. 3. Interdiffusion coefficient as a function of the annealing temperature for QW2 (4 nm) of the GaAs/AlGaAs structure. The solid and dashed lines are linear fits of the data of the samples capped by undoped and P-doped SOG films, respectively.

this Arrhenius plot $D = D_0 \exp(-E_a/kT)$, the activation energy, E_a , was calculated to be 4.8 ± 0.6 and 4.1 ± 0.4 eV for undoped and P-doped SOG encapsulated samples, respectively. These values are typical of the IFVD processes.¹³⁻¹⁵

It is found¹⁶ that, for undoped SOG film, by varying the baking temperature (from 210 to 505 °C), the SOG film properties changed. At higher curing temperature (>300 °C), the density of the pores in the SOG film was enhanced, resulting in correspondingly increased interdiffusion in the GaAs/AlGaAs QWs. Similar results were obtained for the samples covered with P-doped SOG films in this study, presented in Fig. 4, and they show the baking temperature dependence of the shift in PL energy of QW2 in the P-doped SOG encapsulated samples which were annealed at 900 °C for 60 s. The shift in energy from the low temperature (100 °C) baked, P-doped SOG capped sample is lower than the higher temperature (250–400 °C) baked samples. However, as also shown in Fig. 4, for all the samples capped with

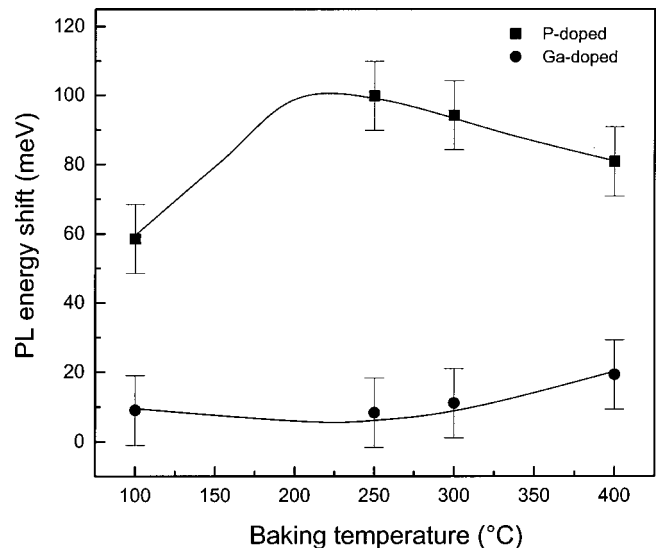


FIG. 4. PL energy shift from the 4 nm QW2 capped with P and Ga doped SOG layers baked at various temperatures and annealed at 900 °C for 60 s.

Ga-doped SOG layers, over the entire region of baking temperatures, small shifts in energy (below 20 meV) were observed, and no obvious dependence on the baking temperature was observed.

The above results unambiguously reveal that the SOG film, which is doped with P, is capable of promoting significant intermixing. This is consistent with the results reported by Rao *et al.*¹⁷ that showed that SiO₂:P (1% P by weight) is able to enhance intermixing although they found that P-doped film has higher disordering efficiency than the undoped film. However, in other work it was reported¹⁸ that SiO₂ doped with 5% P by weight could substantially suppress intermixing in laser structures. Two explanations were proposed by those authors to explain the suppression. First, 5 wt % P may be able to cause dramatic changes in the SiO₂:P films, making it denser and less porous than SiO₂. Second, the addition of P to the SiO₂ film led to an increase in the thermal expansion coefficient and thus to a change in strain during annealing which was also supposed to reduce Ga out-diffusion. Apparently, the amount of P that is doped in the SiO₂ is a very important parameter. Although it was found that 1 wt % P did not drastically change the properties of SiO₂:P compared with SiO₂, the presence of P doping enhanced the disordering efficiency by giving rise to enhanced Ga solubility.¹⁷ For the case of the P-doped SOG films used in our study, according to the doping density of $5 \times 10^{19} \text{ cm}^{-3}$ P atoms in the SOG film specified by the supplier, the content of P in the SOG film may have been as low as ~ 0.11 wt %. This would neither vary the SiO₂ film properties nor enhance the Ga solubility substantially, and would lead to similar intermixing behavior to that in the undoped SOG film. It indicates that the doping concentration of P in the SiO₂ layer is one of the key parameters which may control whether intermixing is either promoted or suppressed. A more systematic doping concentration study of P-doped spin-on silica is worth being carried out to clarify this further.

On the other hand, all the results demonstrate that Ga-doped SOG film is capable of significantly suppressing intermixing without any variation in the baking/annealing conditions. It is known that, for GaAs/AlGaAs material, the IFVD process is essentially a result of the high solubility of Ga in the SiO₂ film. During annealing, Ga atoms in the GaAs/AlGaAs structure are able to outdiffuse into the SiO₂ capping layer leaving behind Ga vacancies which in turn promote intermixing. However, when the SiO₂ was doped with Ga, the diffusion gradient driving the outdiffusion of Ga atoms from GaAs into the capping layer was greatly decreased. Furthermore, doping with Ga may increase the thermal expansion coefficient of the SOG film which is also unfavorable for the interdiffusion process due to the thermal stress effect.¹⁹ A combination of both effects led to significant suppression of intermixing in the structure. In fact, as early as 1981, was the suppression of Ga diffusion into the Ga-doped SOG layer observed by Auger electron spectroscopy, and it was applied to obtain the metal-insulator-semiconductor diodes whose capacitance approaches the level of insulators under reverse-bias conditions at low measurement frequencies.²⁰ It is worth mentioning that, compared with other dielectric films which have been proposed as inhibiting

intermixing, such as SrF₂, BaF₂, CaF₂, or MgF₂,^{21,22} the Ga-doped SOG film does not have any problems in processing, such as cracking, or difficulties in removal after annealing. Obviously, it could be an ideal cap layer for the prevention of intermixing used in combination with other intermixing promoting layers to achieve device integration.

In summary, the doping effects of the spin-on silica films on quantum-well intermixing have been studied in GaAs/AlGaAs quantum-well structures. The films doped with P were able to enhance intermixing in a manner similar to that in undoped SOG films. However the Ga-doped silica films were found to suppress intermixing significantly. Further work is still underway to investigate the doping concentration effect of both dopants, P and Ga, on the degree of intermixing and hence make it more controllable quantitatively. Nevertheless, all the results clearly suggested that Ga-doped SOG film is very promising for use as a protecting cap layer for optoelectronic device integration.

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