Suppression of quantum well intermixing in GaAs/AlGaAs laser structures using phosphorus-doped SiO_2 encapsulant layer

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A phosphorus-doped silica (SiO_2:P) cap containing 5 wt% P has been demonstrated to inhibit the bandgap shifts of *p-i-n* and *n-i-p* GaAs/AlGaAs quantum well laser structures after rapid thermal processing. The intermixing suppression has been attributed to the fact that SiO_2:P is more dense and void free compared with standard SiO_2 together with a strain relaxation effect of the cap layer during annealing. Band gap shift differences as large as 100 meV have been observed from samples capped with SiO_2 and with SiO_2:P. The *n-i-p* structure showed a higher degree of intermixing compared to *p-i-n* structure. This behaviour has been attributed to the rise of Fermi level in the *n* doped structure, through which the formation energy of Ga vacancies is reduced compared to the *p* doped structure. © *1997 American Institute of Physics.* [S0021-8979(97)02105-1]

SiO_2 thin films have been used extensively to achieve impurity free vacancy induced disordering (IFVD),[1] by promoting out-diffusion of gallium into the cap layer during annealing, in GaAs/AlGaAs quantum well (QW) structures. As arsenic from GaAs surface layers evaporates at annealing temperatures around 700 °C,[2] a dielectric mask is required both to preserve the surface quality of the samples and to achieve selective intermixing across a wafer during the annealing step.

A number of masking dielectric materials or techniques have been reported, most notably using SrF_2,[3] Si_3N_4,[4] and a hydrogen passivation technique.[5] SrF_2 is an effective mask for QW intermixing suppression and has been used in conjunction with SiO_2 caps to fabricate photonic integrated devices such as extended cavity lasers[6] and integrated passive waveguides for distributed Bragg reflectors.[7] In addition, SrF_2 masks have also been used to spatially control the degree of intermixing across a wafer. Band gap tuned lasers, fabricated on a single chip and four-wavelength channel waveguide photodetectors have been demonstrated using this technique.[8] However, in our experience, a SrF_2 mask induces damage and cracks, due to thermal stress on the GaAs surface when the annealing temperature is higher than 930 °C, limiting the maximum degree of selective intermixing achievable in the GaAs/AlGaAs system. High purity Si_3N_4 films are difficult to obtain because of the systematic incorporation of O_2 in the film, resulting in SiO_xN_y, although this can be an effective cap for inducing Ga out-diffusion.[9] A hydrogen passivation technique has recently been demonstrated as an effective mask for QW intermixing suppression in undoped structures.[4] The main limitation of this technique is that it is only effective at relatively low temperatures (900 °C), and the possibility of transferring this technique to the more common doped *p-i-n* laser structures used in optoelectronics is still under investigation.

Recently, the use of a SiO_2 layer doped with phosphorus (SIO_2:P) has been reported by Rao *et al.*[10] to be a ‘‘universal’’ intermixing source for III-V compounds. SiO_2:P with 1% by weight of P[11] was used to induce intermixing in nominally undoped GaAs/AlGaAs shallow multiple QW structures by furnace annealing at a relatively low temperature (850 °C), and therefore a masking dielectric cap to prevent intermixing and for surface protection was not required during annealing.

In this paper, we demonstrate that SiO_2 doped with 5 wt% P can be used effectively to suppress the out-diffusion of Ga, and hence can selectively mask intermixing in *p-i-n* and *n-i-p* GaAs/AlGaAs double QW laser structures. In this study encapsulants with a higher P content were not considered due to their increasingly hygroscopic nature[12] affecting the IFVD process reliability, whereas standard undoped SiO_2 layers were used as intermixing sources. Large differential shifts between regions masked with SiO_2 and SiO_2:P have been observed with excellent surface morphology and a high degree of reproducibility. Both layers can be removed easily and effectively using a buffered HF solution. The results imply that SiO_2:P can be used in conjunction with SiO_2 to achieve selective intermixing across a wafer. We also looked at the effect of SiO_2 induced QW intermixing on *p-i-n* and *n-i-p* structures and it was found that *n-i-p* structures exhibit a higher degree of intermixing compared to *p-i-n* structures.

Two wafers having a similar, separate confinement heterostructure configuration were grown by molecular beam epitaxy in the form of *p-i-n* and *n-i-p* double QW laser structures. The *p-i-n* wafer consisted of a 0.5 μm GaAs buffer layer grown on a Si doped *n*-type GaAs substrate. The DQW region was undoped and consisted of two 10 nm wide GaAs quantum wells, separated by a 10 nm $Al_{0.2}Ga_{0.8}As$ barrier. The top and bottom $Al_{0.2}Ga_{0.8}As$ barriers were 0.1 μm thick. Both the upper and lower cladding $Al_{0.4}Ga_{0.6}As$ layers were

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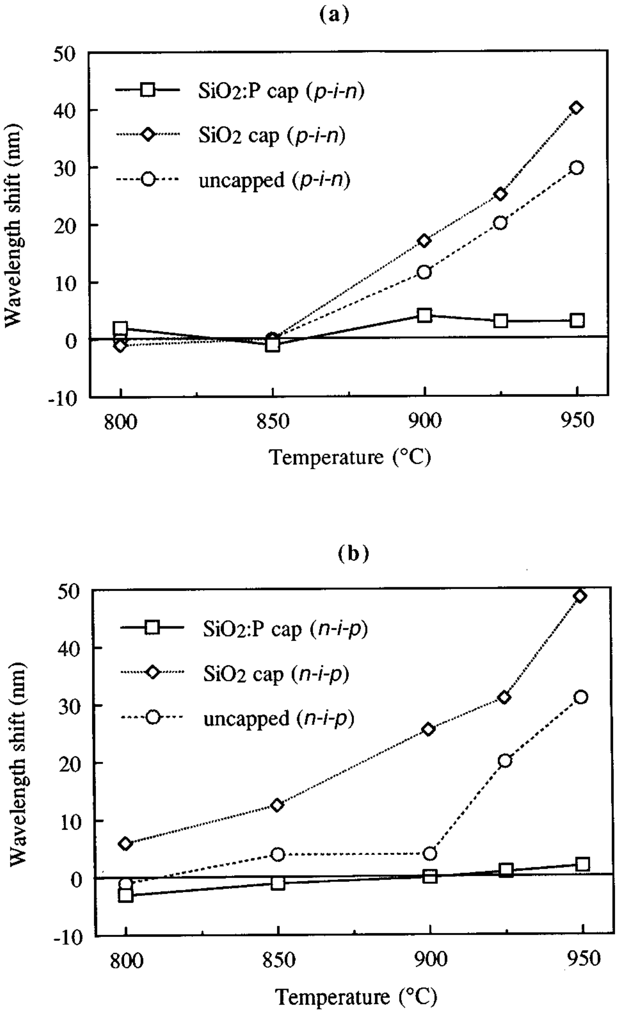

FIG. 1. Wavelength shifts of the 77 K PL peak for SiO_2 capped, SiO_2:P capped and uncapped (a) *p-i-n* and (b) *n-i-p* samples as a function of annealing temperature with a duration of 60 s.

1.5 μm thick and doped at a concentration of 5×10^{17} cm^{-3} using Be and Si respectively. The top contact layer consisted of 0.1 μm of GaAs doped with 5×10^{18} cm^{-3} of Be. The structure of the *n-i-p* wafer was similar to the *p-i-n*, apart from the fact that a semi-insulating GaAs substrate was used and the growth sequence was the opposite.

Dielectric films of SiO_2 and SiO_2:P, both having a thickness of 200 nm, were deposited at a temperature of 330 °C using a conventional plasma enhanced chemical vapour deposition (PECVD) apparatus equipped with a separate PH_3 flow line for P doping. The P content was measured by energy dispersive x-ray (EDX) spectroscopy on a 200 nm thick layer of SiO_2:P deposited, using the same PECVD system and in the same experimental conditions, on a Si wafer. A low accelerating voltage (6 keV) and beam current (0.5 nA) was used to reduce the penetration depth and probe the SiO_2:P film only, giving a P content of 5% by weight, with a 1:2 ratio between Si and O. After deposition of the oxides, the samples were cleaved into squares of area 2×2 mm^2 and rapid thermal annealed for 60 s in flowing N_2 at temperatures between 800°C to 950°C. Uncapped samples were annealed at the same time to study the thermal stability of the wafer. Samples were sandwiched face-down between two pieces of fresh GaAs to provide proximity capping during annealing. Photoluminescence (PL) measurements at 77 K were performed on the annealed samples to assess the degree of intermixing.

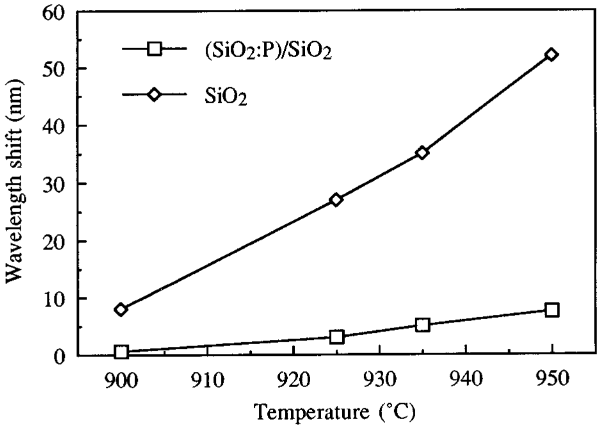

FIG. 2. Wavelength shifts of the 77 K PL peak for *p-i-n* MOCVD samples partially masked with SiO_2:P and capped with SiO_2 as a function of annealing temperature with a duration of 60 s.

The blue wavelength shifts in the 77 K PL peak, as compared with the as-grown material, versus the anneal temperature for the *p-i-n* and *n-i-p* structures are shown in Figures 1(a) and (b) respectively. It is noted from these figures that SiO_2:P acts as a very effective mask for preventing Ga out-diffusion, limiting the band gap widening to no more than 5 nm for both *n-i-p* and *p-i-n* structures at temperatures up to 950 °C. Moreover, no surface damage was produced by this dielectric cap under the annealing conditions studied here. In contrast, the blue shifts for both *p-i-n* and *n-i-p* samples capped with SiO_2 increase with temperature and are always greater than those for uncapped samples, demonstrating the enhanced disordering promoted by SiO_2 capping as compared with uncapped samples.

To further validate our experiments, the SiO_2:P film was partially removed from *p-i-n* double QW laser samples, cleaved from a metal organic chemical vapor deposition (MOCVD)-grown wafer, using optical lithography and wet etching in buffered HF solution, and the samples were capped with 200 nm of SiO_2 and rapid thermal annealed under the conditions described above. Figure 2 shows the PL shift versus the annealing temperature and again the masking properties of the SiO_2:P film are quite evident. It can be witnessed here that differential band gap shifts larger than 40 nm can be easily obtained in samples partially masked with SiO_2:P and capped with SiO_2, with excellent surface morphology, in particular at the edge interface between SiO_2:P and SiO_2. In fact this new masking technique has been used to fabricate high quality extended cavity ridge lasers on *p-i-n* material with very low losses.[13]

There are at least two possible explanations for the masking properties of SiO_2:P films. First, it is well known that SiO_2:P films are more dense and void-free than SiO_2.[12] Films of SiO_2:P with a weight ratio P_2O_5/SiO_2 of 4% have been used[14] as a capping material for open-tube thermal activation of Si implants in GaAs and it has been found that the diffusion coefficient of implanted Si in semi-insulating GaAs is about one order of magnitude smaller for SiO_2:P than for SiO_2. This was attributed to the presence of a reduced number of group III vacancies due to less Ga out-diffusion. Second, due to the difference in thermal expansion coefficients at the annealing temperature, a strain effect exists at the interface between GaAs and SiO_2 during the annealing stage. The thermal expansion coefficient of GaAs is about ten times larger than SiO_2 and as a consequence the SiO_2 film is under tensile strain and the GaAs surface layer is under compressive strain. Under this condition, because of the high diffusion coefficient of Ga in SiO_2, the out-diffusion of Ga atoms into the SiO_2 film is an energetically favourable process because it minimises the strain in the system. The addition of P into the SiO_2 film leads to an increase in the thermal expansion coefficient[12] and a decrease in the glass softening temperature.[15] Therefore, less compressive strain will be induced during the annealing step in the GaAs surface layer and, as a result, the number of Ga vacancies will be reduced due to less Ga out-diffusion.

For the above reasons and from our experimental results we postulate that a SiO_2:P film with 5 wt% P prevents Ga out-diffusion, and hence QW intermixing, during annealing whereas SiO_2, as is generally accepted and experimentally demonstrated, promotes it. Moreover, based on the above arguments, we propose that surface strain induced by dielectric caps plays an important role in the IFVD process.

Our results do not conflict with those reported by Rao *et al.*[10] because the addition of small amounts of P (1 wt%) does not drastically change[12] the properties of SiO_2:P as compared with SiO_2 and hence both caps can have a promoting effect on intermixing.

It is noted from Figs. 1(a) and (b) that *p-i-n* and *n-i-p* wafers have similar degrees of intrinsic thermal stability since the uncapped samples from these wafers shifted to about the same wavelength under similar annealing conditions. Comparing Figs. 1(a) and (b) shows that SiO_2 capped *n-i-p* samples exhibited larger degrees of QW intermixing than the *p-i-n* samples. This may be due to the crystal Fermi level effect,[16] through which the equilibrium Ga vacancy concentration is larger in *n*-type material than in *p*-type material due to a reduction in the formation energy of group III vacancies. In the *n-i-p* sample, the *n* doped contact and top cladding layers support Ga vacancies generated by the SiO_2 layer, hence larger degrees of intermixing were observed. From the integrated photonic devices point of view, the above results suggest that the growth of *n-i-p* structures would give a higher degree of intermixing than conventional *p-i-n* structures typically used in QW intermixing processes.

In summary, we have investigated the QW intermixing effects of 5 wt% P-doped SiO_2 and undoped SiO_2 on *p-i-n* and *n-i-p* GaAs/AlGaAs structures. The SiO_2:P film has been successfully used to suppress the bandgap shift for both *n-i-p* and *p-i-n* structures. This is attributed to the fact that SiO_2:P is more dense and void-free as compared with standard SiO_2 together with a strain relaxation effect of the cap layer during annealing resulting in less Ga out-diffusion. SiO_2:P containing 5 wt% P appears to be a better intermixing mask than SrF_2 since it can be easily removed and induces no damage to the surface after the QW intermixing stage. From the studies carried out on the IFVD process, we confirm that the diffusion of the group III vacancy is supported in *n*-type samples. This study also suggests that a larger degree of intermixing can be obtained through the use of *n-i-p*, rather than *p-i-n*, structures when using the IFVD process.

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