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Citation: [Applied Physics Letters](#) **80**, 4351 (2002); doi: 10.1063/1.1484244

View online: <http://dx.doi.org/10.1063/1.1484244>

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Impurity-free disordering mechanisms in GaAs-based structures using doped spin-on silica layers

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(Received 11 January 2002; accepted for publication 11 April 2002)

We have used photoluminescence, deep level transient spectroscopy and x-ray photoelectron spectroscopy to investigate the mechanisms of impurity-free disordering in GaAs-based structures using doped spin-on silica layers. We demonstrate that V_{Ga} is efficiently converted into arsenic-antisite, As_{Ga} , related defects (EL2-type defects) when the GaAs layer is under compressive stress. We propose that the efficient formation of EL2-type defects reduces the efficiency of impurity-free interdiffusion of GaAs/AlGaAs quantum wells. © 2002 American Institute of Physics. [DOI: 10.1063/1.1484244]

Impurity-free disordering (IFD) using dielectric capping layers has been used to modify the optical properties of GaAs-based materials for monolithic integration of devices with different functionalities.¹ This process introduces defects related to gallium vacancies, V_{Ga} , arsenic interstitials, As_i , and arsenic antisites, As_{Ga} (i.e., EL2-type defects) in GaAs.^{2,3} We have also shown recently that the introduction of these defects is influenced by the stress imposed by the dielectric layer on the GaAs layer at the annealing temperature.⁴ In GaAs-based structures, IFD is a two-step mechanism, including the creation of V_{Ga} by outdiffusion of Ga atoms into the capping layer, and the diffusion of V_{Ga} away from the capping layer–GaAs interface.⁵ Experimental evidence shows that the second step is stress dependent.^{5–7} However, the relative importance of the two steps is not known.

Doped plasma-enhanced chemical vapor deposited SiO_2 (Ref. 8) and spin-on glass (SOG) (Refs. 9–11) layers have been used to control the extent of interdiffusion of GaAs-based structures. These silica layers are inexpensive and readily available commercially, and their properties, including porosity and doping, can be controlled. The relative importance of the two steps that drive disordering in GaAs-based structures can be addressed by using doped and undoped SOG. In this letter, we demonstrate that V_{Ga} vacancies created by the outdiffusion of Ga atoms into the silica capping layer may not contribute to the interdiffusion process if they are efficiently converted into EL2-type defects.

Epitaxial GaAs layers of (100) orientation doped with

$1 \times 10^{16} \text{ Si/cm}^3$ were grown by metalorganic chemical vapor deposition (MOCVD). The epitaxial layers were spin coated with undoped, P-doped, and Ga-doped silicate SOG at 3000 rpm for 30 s. The samples were baked at 400 °C for 15 min before rapid thermal annealing (RTA) at 900 °C for 30 s under Ar flow. Details of Schottky barrier fabrication and deep level transient spectroscopy (DLTS) measurements have been described previously.^{2–4} X-ray photoelectron spectroscopy (XPS) was used to study the outdiffusion of Ga into the SOG layers. We used a VG ESCALAB 220-*i*XL spectrometer using monochromatized Al $K\alpha$ x rays and an Ar-ion gun for in-depth profiling. The in-depth profiles of O, Si, Ga, As, and P were measured by recording the O 1s, Si 2p, Ga 2p_{3/2}, As 3d, and P 2p photoelectron spectra, respectively. SOG-induced impurity-free interdiffusion of a GaAs/AlGaAs structure that contains two quantum wells (QWs) was investigated by low-temperature photoluminescence (PL). The nominal thickness of the QWs was 2.3 nm (QW1, closer to surface) and 4.0 nm (QW2), and they were separated by 50 nm $\text{Al}_{0.54}\text{Ga}_{0.46}\text{As}$ barriers.

Figure 1 illustrates the PL spectra obtained from uncapped (dotted line) and oxide capped (solid line) samples with undoped, P-doped, and Ga-doped SOG layers following RTA at 900 °C for 60 s. Two clearly resolved excitonic peaks that correspond to $n=1$ electron to heavy-hole transitions in the two QWs are observed in each case. The emission wavelength of the capped and annealed QWs is blueshifted, with the effect being most pronounced for P-doped SOG and least for Ga-doped SOG. The blueshift in excitonic emission from QWs is the result of the increase in band gap of GaAs QWs following Al–Ga interdiffusion across the barrier–well interface.^{1,5–11} It is worth noting here that the larger blueshift for

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FIG. 1. PL spectra (solid curves) of the samples capped with (a) undoped, (b) P-doped, and (c) Ga-doped spin-on silica layers baked at 400 °C for 15 min and annealed at 900 °C for 60 s. Spectra shown by dotted curves are from uncapped annealed samples (references).

QW2 from P-doped SOG compared to undoped SOG is consistent with the results of Rao *et al.*,¹² but is in contrast to those of Cusumano *et al.*⁸

Figure 2 shows the XPS in-depth profiles of Ga, O, Si, As, and/or P in undoped, P-doped, and Ga-doped SOG layers. Figure 2(a) reveals the outdiffusion of Ga atoms into the undoped SOG, with most segregation taking place on the oxide side of the SOG/GaAs interface. This result is in qualitative agreement with the PL results in Fig. 1(a). The GaAs layer is under compressive stress during RTA, which makes the outdiffusion of Ga atoms into the SOG layer thermodynamically favorable.⁵ A comparison of Figs. 2(a) and 2(c) may explain the suppression of interdiffusion by the Ga-doped SOG layer. The Ga-doped SOG contains 6%–7% Ga after RTA. We have not observed any marked differences between the distributions of Ga within the Ga-doped SOG before and after RTA. Since this concentration exceeds the concentration of outdiffused Ga into the undoped SOG [Fig. 2(a)], there is a diffusion barrier against the segregation of Ga atoms into the Ga-doped SOG layer. Consequently, the interdiffusion process is suppressed as shown in Fig. 1(c). However, the slight blueshifts in PL emission of IFD QWs suggests that chemical reactions between GaAs and Ga-doped SOG in a region confined to the SOG/GaAs interface may still produce some V_{Ga} .

Figure 2(b) shows that the P-doped SOG layer contains ~0.4% phosphorus after annealing. The doping concentration in our P-doped SOG is very similar to that used by Rao *et al.*,¹² but is about one order magnitude smaller than the P doping used by Cusumano *et al.*⁸ We can, therefore, con-

FIG. 2. XPS in-depth profiles of Ga, Si, O, As, or P in (a) undoped, (b) P-doped, and (c) Ga-doped spin-on silica layers annealed at 900 °C. The outdiffusion of Ga into the silica capping layers was measured by monitoring the Ga $3p_{3/2}$ photoelectron spectrum. The Ga in the oxide layers is bonded to oxygen.

clude that the concentration of phosphorus in P-doped SOG layers is a critical parameter to consider when designing IFD studies. Both the porosity of the SOG layer and the compressive stress that it imposes on the GaAs structure are expected to decrease with an increase of P doping.⁸ Rao *et al.*¹² have attributed the larger interdiffusion in their QW structures by P-doped SOG compared to an undoped layer to increased solubility of Ga atoms in the former layer, but did not provide any experimental evidence to support their argument. A comparison of the results shown in Figs. 2(a) and 2(b) clearly demonstrates that this is not the case. Although there is outdiffusion of Ga atoms into the P-doped layer [Fig. 2(b)], the segregation effect is less than in undoped SOG [Fig. 2(a)]. Based on these results alone one would expect a larger concentration of V_{Ga} , and hence larger interdiffusion, to be produced with undoped SOG. The results shown in Figs. 1 and 2 unambiguously show that although interdiffusion is related to the outdiffusion of Ga atoms into the capping layer, other processes, which have not been identified thus far, determine the extent of disordering.

In order to explain our results, we have studied the defects created in rapid thermally annealed *n*-GaAs epitaxial layers capped with the undoped and doped SOG layers. Figure 3 illustrates DLTS spectra after RTA for *n*-GaAs capped with undoped (dashed line), P-doped (solid line), and Ga-doped (dotted line) SOG layers. IFD created four electron traps $S1$ ($E_C - 0.23$ eV), $S2$ ($E_C - 0.46$ eV), $S3$ ($E_C - 0.72$ eV), and $S4$ ($E_C - 0.74$ eV). The concentration of defects created by Ga-doped SOG is similar to that obtained

FIG. 3. DLTS spectra obtained from disordered *n*-type GaAs epitaxial layers using undoped (dashed curve), P-doped (solid curve), and Ga-doped (dotted curve) spin-on glass capping layers. The samples were annealed at 900 °C under Ar flow following baking of the silica layers at 400 °C for 15 min. The region between 0.35 and 0.57 μm was probed in all samples by adjusting the quiescent and filling biases.

when the *n*-GaAs epilayer is annealed without any dielectric capping.² This is in good qualitative agreement with the results shown in Figs. 1(c) and 2(c).

Of more interest are the differences between the defect rates of introduction by undoped and P-doped SOG layers. The concentration of S4 is higher in the *n*-GaAs layer disordered using undoped SOG compared to P-doped SOG, whereas both S1 and S2 show the reverse effect. We have recently provided evidence that S4 is a member of the EL2 family of defects.^{2,3} During RTA the GaAs layer is under compressive stress,⁵ and the formation of As_i and, consequently, As_{Ga} ($V_{\text{Ga}} + \text{As}_i \rightarrow \text{As}_{\text{Ga}}$) is favored. As for S1 and S2, we have proposed that they are related to complexes that involve As_i and V_{Ga} . In particular, we have tentatively identified S2 as the $V_{\text{Ga}}\text{-Si}_{\text{Ga}}$ complex.^{2,3} In light of the results shown in Figs. 2 and 3, we propose that although more V_{Ga} may be initially produced by the larger outdiffusion of Ga atoms into the undoped compared to the P-doped SOG layer, a larger fraction of these V_{Ga} is efficiently converted into the EL2-type defect S4 in the former situation. On the other hand, the lower outdiffusion of Ga atoms into the P-doped layer can be explained by a higher density of the P-doped layer coupled with a stress relaxation effect of this layer during annealing.⁸ This reduced compressive stress also makes the formation of As_{Ga} , and hence S4, less energetically favorable. Consequently, relatively more V_{Ga} is retained as shown by the larger concentration of S2 obtained from disordering using the P-doped layer compared to the undoped SOG (Fig. 3).

In light of the results in Figs. 2 and 3 and the above discussion, we are now able to explain the results of impurity-free interdiffusion of GaAs/AlGaAs QWs depicted

in Fig. 1. The Ga-doped SOG layer effectively suppresses interdiffusion because the creation of V_{Ga} is efficiently suppressed. On the other hand, the largest outdiffusion of Ga atoms is observed in the undoped SOG layer, and yet the extent of interdiffusion is either similar to (QW1) or lower than (QW2) that for the P-doped SOG layer. Although the undoped layer may produce a larger concentration of V_{Ga} than the P-doped SOG layer, the higher compressive stress imposed on the GaAs layer by the undoped SOG layer during RTA also results in the efficient conversion of V_{Ga} into As_{Ga} -type defects. Essentially, the higher concentration of V_{Ga} which is retained when using P-doped SOG layer produces a larger Ga-Al interdiffusion. Our results suggest that the compound effect of the creation of V_{Ga} and the conversion into As_{Ga} under compressive stress is depth dependent, as demonstrated by the different extent of blueshifts in QW1 and QW2 [Figs. 1(a) and 1(b)].

In summary, we have used photoluminescence spectroscopy, x-ray electron spectroscopy, and deep level transient spectroscopy to study the impurity-free disordering process in GaAs-based structures using undoped and doped spin-on silica layers. We have shown that the extent of impurity-free disordering of GaAs-based structures does not depend only on the creation of V_{Ga} but, maybe more importantly, on their conversion into As_{Ga} -related defects. Our results have highlighted that a better understanding of the defect reactions related to impurity-free disordering of III-V semiconductors may indeed yield the operative mechanisms behind the interdiffusion process.

Two of the authors (P.N.K.D. and H.H.T.) gratefully acknowledge financial support by the Australian Research Council.

¹For a comprehensive review of impurity-free vacancy interdiffusion, see, for example, *Semiconductor Quantum Wells Intermixing*, Optoelectronic Properties of Semiconductors and Superlattices, Vol. 8, edited by E. H. Li (Gordon and Breach, Amsterdam, 2000).

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