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Suppression of interdiffusion in GaAs/AlGaAs quantum-well structure capped with dielectric films by deposition of gallium oxide

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In this work, different dielectric caps were deposited on the GaAs/AlGaAs quantum well (QW) structures followed by rapid thermal annealing to generate different degrees of interdiffusion. Deposition of a layer of Ga$_2$O$_3$ on top of these dielectric caps resulted in significant suppression of interdiffusion. It was found that although the deposition of Ga$_2$O$_3$ and subsequent annealing caused additional injection of Ga into the SiO$_2$ layer, Ga atoms were still able to outdiffuse from the GaAs QW structure during annealing, to generate excess Ga vacancies. The suppression of interdiffusion with the presence of Ga vacancies was explained by the thermal stress effect which suppressed Ga vacancy diffusion during annealing. It suggests that Ga$_2$O$_3$ may therefore be used as a mask material in conjunction with other dielectric capping layers in order to control and selectively achieve impurity-free vacancy disordering.© 2002 American Institute of Physics. [DOI: 10.1063/1.1503857]

I. INTRODUCTION

Over the past several years, as a powerful postgrowth technique, quantum well intermixing (QWI) has been studied extensively. QWI happens through the compositional intermixing (interdiffusion) of the well and barrier atoms in the III–V heterostructure, due to the thermal diffusion of point defects (vacancies or interstitials). Among the various techniques used to create intermixing, impurity free vacancy disordering (IFVD) has been considered to be the most promising technique for device applications due to its simplicity, low optical losses, and low residual damage. However, to realize the monolithic integration of optoelectronic (or photonic) components of different band gap energies across the wafer, which is the main purpose and advantage of QWI, it is essential for the method of intermixing itself to have area selectivity. Unlike ion implantation which is spatially selective, selectivity for IFVD can only be achieved by applying a capping layer which promotes intermixing and another capping layer which prevents intermixing to different regions of the sample. Usually, SiO$_2$ is used to induce IFVD and Si$_3$N$_4$ is used to inhibit intermixing. However, some experiments pointed out that under certain deposition conditions, Si$_3$N$_4$ also enhanced interdiffusion. Recently, much effort has been made to find a way to suppress and thus control intermixing. For example, some studies found that by modifying the properties of the dielectric caps, intermixing could be suppressed. On the other hand, it was proposed that by depositing a dielectric film onto the GaAs surface of a quantum well (QW) structure, the mismatch in thermal expansion coefficient between these two materials will cause thermal stress at the near-interface regions of dielectric film and QW structure during the annealing process. The type of the thermal stress (whether it is compressive or tensile) generated at the surface of the QW structure will in turn affect the diffusion of Ga vacancies and the extent of intermixing. However, although this thermal stress issue was also considered as a factor affecting IFVD by other researchers, no detailed study has been further reported. To confirm the role of thermal stress in the IFVD process and thus to use it to realize selectivity and controllability of IFVD, in this work, a layer of Ga$_2$O$_3$ was deposited onto the GaAs/AlGaAs QW structures which were predeposited with different dielectric films, including SiO$_2$, Si$_3$N$_4$, and spin-on glass (SOG). The Ga$_2$O$_3$ layer was selected since the thermal expansion coefficient of Ga$_2$O$_3$ is $7.3 \times 10^{-6}$ °C (obtained by averaging the thermal expansion coefficients along $a$ and $c$ axes of $\alpha$-Ga$_2$O$_3$) which is larger than those of the predeposited dielectric films and even GaAs. It was found that in all cases, with the deposition of Ga$_2$O$_3$ layers, interdiffusion was significantly suppressed in the QWs after annealing. To reveal the reason for the suppression of interdiffusion, two possibilities are considered: the suppression of Ga outdiffusion from QW structure to the dielectric film (predeposited)
due to the deposition of Ga$_2$O$_3$ layer which may provide additional source of Ga to saturate the dielectric layer; or the suppression of vacancy diffusion due to the change of the thermal stress in the QW structure as a result of the large thermal expansion coefficient of the Ga$_2$O$_3$ layer. X-ray photoelectron spectroscopy (XPS) and cross-sectional transmission electron microscopy (XTEM) measurements were carried out to clarify this problem.

II. EXPERIMENTS

The QW structure used in this experiment was grown on a semi-insulating (100) GaAs substrate by metalorganic chemical vapor deposition (MOCVD). It consisted of four GaAs QWs, $QW_1$, $QW_2$, $QW_3$, $QW_4$ with different thicknesses, 1.4, 2.3, 4.0, 8.5 nm (from surface). Each QW was sandwiched between two 50 nm Al$_{0.54}$Ga$_{0.46}$As barriers. The structure was then terminated with a 40 nm GaAs capping layer to prevent oxidation of the Al$_{0.54}$Ga$_{0.46}$As layer. All layers were undoped and grown at 750 °C. Three pieces of 1 cm$^2$ samples were cleaved from the wafer, deposited with three types of dielectric films, SiO$_2$, Si$_3$N$_4$, and spin-on glass, to the thickness of 150–200 nm. Both SiO$_2$ and Si$_3$N$_4$ were deposited by plasma enhanced chemical vapor deposition (PECVD) using N$_2$O/SiH$_4$ and NH$_3$/SiH$_4$ flow, respectively, at 35 °C. The SOG film was formed by spinning commercial liquid silica on the sample surface at a speed of 3000 rpm for 30 s followed by subsequent baking at 400 °C for 15 min. Half of each dielectric film capped sample were then covered with ~90 nm Ga$_2$O$_3$ by MOCVD using N$_2$O and trimethylgallium as sources at a temperature of 600 °C for 20 min. As to the other half of the sample, the dielectric film was etched off in 10% HF to provide an uncapped reference region. All the samples were then rapidly thermally annealed (RTA) at 900 °C for 60 s. During annealing, the etched samples were protected from excessive loss of As by using the proximity capping technique. Low temperature (12 K) photoluminescence (PL) was performed using a green He–Ne laser (543.5 nm) as excitation source and the signal was detected by silicon charge coupled device through a 0.27 m monochromator. XPS (using a VG ESCALAB 220-iXL spectrometer with the monochromated Al $K\alpha$ x-ray source) and XTEM (using a Philips CM 300 microscope) measurements were performed on selected samples.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the PL spectra from four samples, (a) as-grown, (b) as-grown+RTA, (c) as-grown+SiO$_2$(PECVD)+RTA and (d) as-grown+SiO$_2$(PECVD)+Ga$_2$O$_3$+RTA. The four peaks in spectrum (a) originate from the four QWs in the structure. It can be seen that after RTA [spectrum (b)], the four peaks are shifted to lower wavelengths due to thermal intermixing and with the SiO$_2$ capping layer [spectrum (c)], they are shifted further, as normally observed in the IFVD process. Meanwhile, the disappearance of the peak from $QW_1$ was observed as a consequence of three possibilities.\(^{18}\) (i) accumulation of nonradiative defect centres in the near-surface region, (ii) complete intermixing of $QW_1$, or (iii) change of well com-
During the deposition and annealing processes, the XPS in-depth profiling was performed using monochromated Al Kα x-ray source and Ar-ion sputtering at 5 keV beam energy. The profiles of O, Si, Ga, and As were measured by recording the O 1s, Si 2s, Ga 2p \(3/2\), and As 3d photoelectron spectra respectively on two Ga\(_x\)O\(_y\) deposited samples: (a) as-grown + PECVD SiO\(_2\) + Ga\(_x\)O\(_y\) (as-deposited), (b) as-grown + PECVD SiO\(_2\) + Ga\(_x\)O\(_y\) (annealed), as shown in Fig. 2. It can be seen from Fig. 2(a) that, prior to annealing, there is already some Ga (~2%–5%) in the SiO\(_2\) layer, which means that during the 600 °C, 20 min deposition process of Ga\(_x\)O\(_y\), Ga atoms were injected from the Ga\(_x\)O\(_y\) and/or QW structure. The Ga\(_x\)O\(_y\) film deposited on our sample is Ga rich with the composition of Ga\(_0.51\)O\(_{0.49}\). After the RTA at 900 °C for 60 s, the film became less Ga rich with the composition of Ga\(_0.51\)O\(_{0.49}\) and a change in the shape of the Ga 2p profile at the SiO\(_2\)/GaAs interface region can be observed, as shown in Fig. 2(b). To examine whether the injection of Ga during the deposition and annealing processes of Ga\(_x\)O\(_y\) layer affected the outdiffusion of the Ga atoms from the QW structure, a close comparison of the Ga 2p and Si 2s spectra between the two Ga\(_x\)O\(_y\) capped samples at the SiO\(_2\)/GaAs interface region is displayed in Fig. 3. The spectra from the sample without Ga\(_x\)O\(_y\) capping (but with SiO\(_2\) and RTA) are also plotted in Fig. 3. Since the total thickness of the dielectric layers is different in these samples, the SiO\(_2\)/GaAs interfaces of all the spectra are normalized to correspond to the sputtering time at 1/e peak value of the Si 2s spectra. It is noted that the concentration of Ga in the SiO\(_2\) layer capped with Ga\(_x\)O\(_y\) before RTA (solid squares) is higher than the level of Ga which the uncapped (by Ga\(_x\)O\(_y\)) SiO\(_2\) (solid triangles) accommodated during our experimental annealing condition. Nevertheless, this does not constitute a restraining force to completely suppress outdiffusion of Ga into the SiO\(_2\)+Ga\(_x\)O\(_y\) stacking layer from the underneath GaAs QW structure. It is clear in Fig. 3 that the annealed Ga\(_x\)O\(_y\) capped sample (solid circles) has a much diffused transition region in the Ga profile at the SiO\(_2\)/GaAs interface compared with that of the un-annealed sample (solid squares). Similar Ga profile with diffused transition region at the interface can also be observed in the sample encapsulated only with SiO\(_2\) (solid triangles). It indicates that although the deposition of Ga\(_x\)O\(_y\) and subsequent annealing caused injection of Ga into the SiO\(_2\) layer, it did not fully saturate the SiO\(_2\) film, at least in a region adjacent to the SiO\(_2\)/GaAs interface. Gallium atoms were still able to outdiffuse from the GaAs QW structure, leaving behind an excess of vacancies which are expected to promote intermixing in addition to thermal intermixing. However, the PL results presented in Fig. 1 (curve d) suggest that even with these vacancies in the sample, a blueshift smaller than the thermally induced intermixing is exhibited. To explain this, thermal stress effect\(^{14}\) during the IFVD process should be considered.

The mechanism of the IFVD process in GaAs-based system can be divided into two steps which happen almost simultaneously: (i) the generation of gallium vacancies (V\(_{Ga}\)), and (ii) the diffusion of V\(_{Ga}\). The main factors which affect the generation of V\(_{Ga}\) are the film quality, the diffusion of native defects and the metallurgical reaction between GaAs substrate and the encapsulant.\(^{11,19}\) The diffusion of V\(_{Ga}\) was proposed to be affected by the stress imposed on the semiconductor by the encapsulant(s) in Ref. 14. When GaAs is under compressive stress, the vacancies generated by outdiffusion of Ga atoms into the encapsulant can be driven to diffuse deeper into the GaAs material to create interdiffusion. However, if the GaAs is under tensile stress, the vacancies will be trapped in the region under stress, making little contribution to interdiffusion. In our experiments, all samples, whether with or without Ga\(_x\)O\(_y\), were processed from the same wafer and subjected to the same annealing conditions.

![FIG. 2. XPS in-depth profiles of Ga, Si, O, and As for the samples which were (a) deposited with both SiO\(_2\) and Ga\(_x\)O\(_y\) (but not annealed) and (b) deposited with both SiO\(_2\) and Ga\(_x\)O\(_y\) and annealed.](image)

![FIG. 3. Normalized XPS in-depth profiles for Ga, Si at the SiO\(_2\)/GaAs interfaces using the sputtering time at 1/e peak value of the Si 2s spectra for the samples which were: as-deposited with both SiO\(_2\) and Ga\(_x\)O\(_y\) (squares), deposited with both SiO\(_2\) and Ga\(_x\)O\(_y\) and annealed (circles), and deposited with only SiO\(_2\) and annealed (triangles).](image)
TABLE II. Thermal expansion coefficient, $\alpha$, of the different materials used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha$(°C$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>$0.52 \times 10^{-6}$</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>$2.8 \times 10^{-6}$</td>
</tr>
<tr>
<td>Ga$_2$O$_3$</td>
<td>$7.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>GaAs</td>
<td>$6.86 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Therefore, no major variation in the concentration of native defects should be expected from one sample to another. The XPS results showed that although the deposition and annealing of Ga$_2$O$_3$ caused additional injection of Ga into the SiO$_2$ film which did change the properties of the SiO$_2$ and may affect the metallurgical reaction at the SiO$_2$/GaAs interface, it did not completely suppress the outdiffusion of Ga from the QW structure. Hence, generation of excess V$_{Ga}$ may have been limited, but surely not totally eliminated. The complete suppression of IFVD after Ga$_2$O$_3$ deposition, especially the partial suppression of thermal intermixing could be correlated only with the change of stress distribution which affects the diffusion of V$_{Ga}$.

As shown in Table II, due to the difference in thermal expansion between GaAs and the dielectric capping film (PECVD SiO$_2$, SOG, or Si$_3$N$_4$), during RTA, GaAs surfaces were all under compressive stress which is favourable for creation and diffusion of vacancies. Therefore, the V$_{Ga}$ generated below encapsulant/GaAs interface diffused under compressive stress to initiate intermixing. However, the compressive stress generated by Si$_3$N$_4$ was obviously smaller than by the other two films, which may lead to a less efficient vacancy diffusion. In addition, Si$_3$N$_4$ film is not porous to Ga or As atoms, whereas SiO$_2$ is known to be a "sink" for Ga atoms. Thus, as illustrated by $E_1$ in Table I, the smallest energy shift was obtained in the sample covered by Si$_3$N$_4$. Between PECVD SiO$_2$ and SOG which have similar thermal expansion coefficients, the extent of interdiffusion depended only on the quality of capping layers. Our previous results$^{20,21}$ have shown that under the experimental conditions used here, SOG (~9% voids) was more porous than PECVD SiO$_2$ (~3% voids). Consequently, more outdiffusion of Ga into the dielectric film and more injection of V$_{Ga}$ into QW structure were expected for SOG than with PECVD SiO$_2$ film. Accordingly, larger PL energy shift was obtained in the SOG encapsulated structure.

With the deposition of Ga$_2$O$_3$ on top of these dielectric films, the situation was different. During high temperature annealing, the overall thermal expansion coefficient of the Ga$_2$O$_3$/SiO$_2$ bilayer$^{22}$ was greatly increased (due to the large value of the Ga$_2$O$_3$’s thermal expansion coefficient), resulting in a much reduced or even eliminated compressive stress in the GaAs surface region below the dielectric film. The V$_{Ga}$, including vacancies generated below the encapsulant/GaAs interface by Ga outdiffusion and some of the grown-in vacancies, could not diffuse into the QW region to promote intermixing. Therefore, as suggested by the negative value of $E_2$ in Table I, no IFVD was obtained. The relationship between stress field distribution and the thermal expansion coefficient has not been established quantitatively yet. However, it is obvious that the stress field distribution in different samples was varied due to combination of different capping layers and as a result, intermixing was suppressed to a different extent (thus different $E_2$). In addition, the exact value of $E_2$ was also determined by the dielectric film quality (which affects the injection of Ga from both the Ga$_2$O$_3$ layer and QW structure) and the grown-in defects in the sample. On the other hand, with the agglomeration of vacancies or other complexes arising from an increase in the As to Ga ratio in the near-surface region of GaAs due to the lack of compressive stress, the quality of the material might be degraded.$^{14}$ Consequently, a reduction in the PL signal intensity was detected, as shown by spectrum (d) in Fig. 1.

XTEM analysis further confirms the earlier results and the proposed mechanism. Figure 4 displays XTEM micrographs of the samples (a) capped with PECVD SiO$_2$, and (b) capped with the same SiO$_2$ and then Ga$_2$O$_3$. Both samples were annealed at 900°C for 60 s. Clearly, in the sample without the Ga$_2$O$_3$ layer, some interdiffusion took place as implied by the blurred interfaces between the 4 QWs and their adjacent barriers, whereas with a Ga$_2$O$_3$ layer the interfaces remained sharp indicating the suppression of intermixing. The GaAs/encapsulant interfaces in Figs. 4(a) and 4(b) are more clearly displayed in the enlargement of the encircled regions. A smooth and uniform dark layer can be observed at the interface in Fig. 4(a), which may be composed of Ga$_2$O$_3$ and As layers$^{23}$ formed due to the Ga atoms outdiffusion and/or their metallurgical reaction with SiO$_2$ during RTA. At the interface displayed in Fig. 4(b), a thinner layer can also be seen and as discussed earlier, this may be due to the suppression of Ga outdiffusion in this sample. Furthermore, a group of defects was observed below the dark layer. These defects were variable in size but had a typical average diameter of ~10 nm. Because of their small size, the nature of the defects could not be determined by electron diffraction. However, they appeared to be very similar to the...

FIG. 4. XTEM micrographs of the sample: (a) deposited with SiO$_2$ and annealed at 900°C for 60 s, (b) deposited with both SiO$_2$ and Ga$_2$O$_3$, and annealed at 900°C for 60 s. The enlargement of the GaAs/SiO$_2$ interface area of (a) and (b), defined by the white circle, is also shown, respectively.
defects observed in the sample capped with a SiO$_2$ + Si$_3$N$_4$ bilayer shown in Ref. 14, where intermixing of QWs was also suppressed. It is likely that the formation of these defects was related to the thermal stress and was responsible for the degradation in PL intensity.

It should be noted that this thermal stress effect occurs only during annealing. No matter whether the as-deposited dielectric film is tensile or compressive, the decisive factor affecting interdiffusion is the thermal stress induced in the GaAs surface by the overall influence of the encapsulants. Therefore, for some of the recent reports on suppression of GaAs interdiffusion using SrF$_2$, BaF$_2$, CaF$_2$, MgF$_2$ capping, or Ge, Al interlayer, $^{24}$ - $^{27}$ it is worth considering carefully the effect of thermal stress in addition to the film quality, metallurgical reactions, and diffusion barrier effects, since all these layers have very different thermal expansion coefficients. Furthermore, new experiments should be designed to systematically study this effect to control intermixing and apply it to the device fabrication.

IV. SUMMARY

It is demonstrated that during the IFVD process, the diffusion of Ga vacancies depends highly on the stress field distribution in the semiconductor material. With the deposition of Ga$_2$O$_3$ on top of the different dielectric films which are commonly used to promote interdiffusion, significant suppression of interdiffusion (especially including component of thermal intermixing) was observed. It was ascribed to the modification of stress field by the large thermal expansion coefficient of Ga$_2$O$_3$, suggesting that this method may be promising in achieving the controlled defect engineering required for any successful application of IFVD.

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1 Quantum Well Intermixing for Photonics, edited by E. H. Li (SPIE, Bellingham, WA, 1997).
17 From the x-ray photoelectron spectroscopic study, it is found that the Ga$_2$O$_3$ films deposited in our experiments are Ga rich. So far we cannot find a report on the thermal expansion coefficients of the Ga$_2$O$_3$ films which have similar compositions as ours. However it is reasonable to presume that the thermal expansion coefficient of Ga-rich Ga$_2$O$_3$ films do not differ greatly from that of Ga$_2$O$_3$.