Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Crystal Growth 272 (2004) 621–626
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Passivation of GaAs surface by ultrathin epitaxial GaN layer

J. Riikonen*, J. Sormunen, H. Koskenvaara, M. Mattila,
M. Sopanen, H. Lipsanen

Optoelectronics Laboratory, Helsinki University of Technology, P.O. Box 3500, FIN-02015 TKK, Finland

---

Abstract

Ultrathin gallium nitride passivation layers grown in situ on near-surface $In_xGa_{1-x}As/GaAs$ quantum wells using metalorganic vapour-phase epitaxy (MOVPE) with dimethylhydrazine as nitrogen source are reported. Nitridation of GaAs using DMHy during the post-growth cool-down is also studied. The effect of passivation on the surface recombination rate of quantum well (QW) structures is characterized using low-temperature (10 K) photoluminescence. Measured after growth, the GaN passivation is shown to enhance the PL intensity of the near-surface QWs approximately by a factor of 20. For samples stored in ambient air for 5 months, the enhancement is nearly 10^3. The results suggest that MOVPE-grown thin GaN layers are applicable to GaAs surface passivation.
© 2004 Elsevier B.V. All rights reserved.

PACS: 78.55.−m; 78.66.−w; 81.15.Gh; 81.65.Rv

Keywords: A1. Photoluminescence; A3. Metalorganic vapor phase epitaxy; A3. Quantum wells; B2. Semiconducting gallium compounds

---

1. Introduction

The high density of surface states of GaAs are known to cause surface Fermi level pinning near the midgap. This is a limiting factor in the performance of advanced electronic and optoelectronic devices, especially in low-dimensional structures. Thus, a variety of different passivation techniques have been studied to solve this problem. GaP formed by As–P exchange reaction, native oxides, standard Si-based insulators (SiO_2 and Si_3N_4), and a variety of plasma nitridation methods, have been demonstrated to passivate GaAs surfaces [1,2]. The use of different plasma methods has faced problems with, e.g., disordered surface leading to deep donor states, and formation of mixture of GaN and Ga_2O_3 instead of pure GaN [3].

Passivation techniques using plasma are ex situ methods for most of the metal organic

---

*Corresponding author. Tel.: +358 9 4515360; fax: +358 9 4513128.
E-mail address: juha.riikonen@hut.fi (J. Riikonen).

0022-0248/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2004.08.110

vapour-phase epitaxy (MOVPE) systems. Although ex situ methods are useful as they can be used during processing, in situ surface passivation has been considered to be the most effective way to reduce the surface state density of epitaxial layers. For example, ultrathin InP layers (1 monolayer, ML) have been shown to be effective in the passivation of AlGaAs/GaAs near-surface quantum wells (QWs) [4–6]. Besides plasma nitridation of GaAs, a thin GaN layer can also be grown epitaxially. The growth of cubic GaN layers on GaAs has been reported despite problems resulting from the large lattice mismatch (~ 20%) between the materials [7,8]. MOVPE growth of epitaxial GaN on GaAs is enabled by the use of dimethylhydrazine (DMHy) as a nitrogen source. The low decomposition temperature of DMHy allows growth at temperatures around 550 °C [9]. Hence, the active structure will not suffer from additional heating during the passivation as the typical growth temperature of GaAs-based materials is around 650 °C.

In this work, we report the epitaxial in situ GaN passivation of GaAs using DMHy precursor as a nitrogen source in a MOVPE reactor. Low-temperature photoluminescence (PL) is used to study the effect of passivation on InGaAs/GaAs QWs. PL intensity enhancements of up to almost three orders of magnitude were measured from GaN-passivated near-surface quantum wells as compared with unpassivated samples.

2. Experimental procedure

The near-surface InGaAs/GaAs quantum well samples were grown in a horizontal MOVPE reactor at atmospheric pressure using hydrogen as the carrier gas. Tertiarybutylarsine (TBAs), trimethylgallium (TMGa), trimethylindium (TMIn), and dimethylhydrazine (DMHy) were used as precursors for arsenic, gallium, indium and nitrogen, respectively. Prior to the growth of the QW structures, semi-insulating GaAs(100) ± 0.1° substrates were annealed in the reactor at 700 °C for 5 min to remove the native oxide. The temperatures mentioned in this report are thermocouple readings [10]. A typical near-surface QW sample consists of a 100 nm thick GaAs buffer layer, an $In_xGa_{1-x}As$ QW and a GaAs top barrier layer. The indium fractions of the 6 and 4 nm thick quantum wells are 20 and 25%, respectively. The thickness of the GaAs cap is 5 nm. The layers were grown at 650 °C and the V/III ratios used for GaAs and $In_xGa_{1-x}As$ were 23 and 10, respectively. The nominal growth rates were 4.2 Å/s for GaAs and 2.7 Å/s for $In_xGa_{1-x}As$ QWs.

Two different surface passivation methods using DMHy were employed on the near-surface quantum wells. In the first method, a thin GaN layer (nominally 1–3 ML) was grown at 550 °C using a V/III molar ratio of 100 to achieve two-dimensional growth [8]. The nominal growth rate of GaN was 1.3 Å/s. In the second method, shown in Fig. 1, after the growth of the top barrier GaAs, the TBAs flow was switched to DMHy at 600 °C to form a thin GaN layer via As–N exchange. After approximately 70 s of cooling, the DMHy protection was switched off at 400 °C. For reference, the same structures were grown without passivation. A deep-QW sample with a 20 nm thick GaAs top barrier layer was also used as a reference.

Diffraction measurements with a high-resolution triple-axis X-ray diffractometer (HR-XRD) with an incident beam monochromator and a mirror were used to determine the growth rate and composition of the $In_xGa_{1-x}As/GaAs$ samples. Low-temperature PL was measured at 10 K using a closed-cycle helium cryostat. A 488 nm line from an argon-ion laser was used for optical excitation. The spectra were recorded with a 0.5 m monochromator and a 77 K Ge p–i–n detector. The surface morphology of the samples was imaged with an atomic force microscope (AFM) using the contact mode.

3. Results and discussion

The PL spectra of the as-grown unpassivated, nitridated, and GaN-passivated 4 nm thick $In_{0.25}Ga_{0.75}As/GaAs$ near-surface QWs with a top barrier thickness of 5 nm are shown in Fig. 2. A deep-QW structure with the top barrier thickness of 20 nm is shown as a reference. The PL intensity of the GaN-passivated sample is

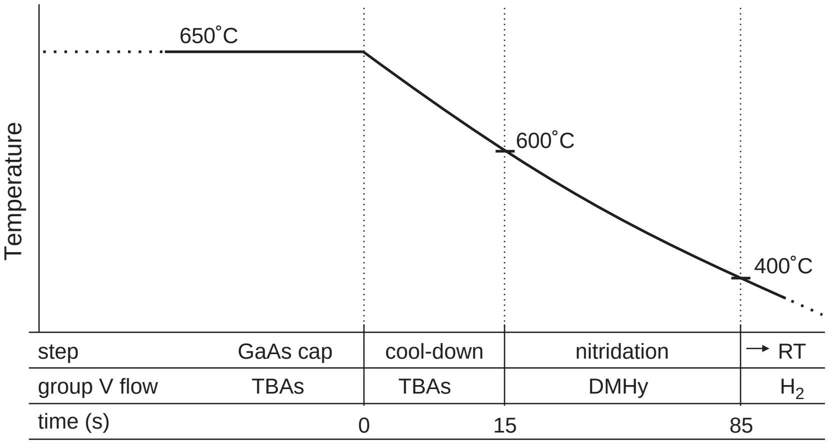

Fig. 1. Schematic plot of the post-growth nitridation procedure (axes not in scale).

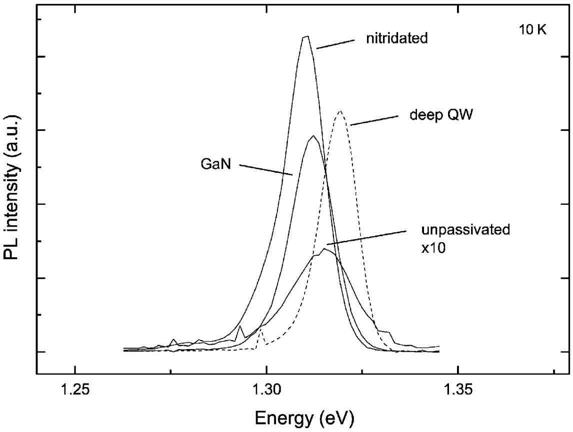

Fig. 2. PL spectra of as-grown passivated 4 nm thick $In_{0.25}Ga_{0.75}As/GaAs$ near-surface QWs. The PL intensities of the passivated samples are enhanced and the peaks are slightly red shifted as compared with the unpassivated QW.

Table 1
Relative PL intensity and energy shift of nitridated, GaN-passivated and deep-QW sample as compared with unpassivated structure. The FWHM of the PL curves are shown for reference. PL spectra of the samples are shown in Fig. 2

Sample	PL intensity	Energy shift (meV)	FWHM (meV)
Nitridated	31	−4.9	12.6
GaN	21	−2.8	13.2
Unpassivated	1	0	19.1
Deep QW	23	4.2	11.3

enhanced by a factor of 21 compared with the unpassivated QW. Table 1 shows the relative PL intensity, energy shift and full-width at half-maximum (FWHM) of the PL spectra in Fig. 2. A small red shift of 2.8 meV can be seen in the PL spectrum of the GaN-passivated quantum well compared with unpassivated structure. This behavior is probably caused by the formation of $GaAs_xN_{1-x}$ on the GaAs–GaN interface due to As–N exchange. As a consequence, the nominally 5 nm thick top barrier GaAs has a graded composition of GaAsN. Thus, the QW barrier is presumably reduced because with low fractions of nitrogen, $GaAs_xN_{1-x}$ has a lower band gap than GaAs. This is seen as a red shift of the PL spectrum. These assumptions are supported by the fact that even a larger red shift (4.9 meV) is evident in the spectrum of $In_xGa_{1-x}As/GaAs$ QW passivated with the nitridation method. It can be expected that in the nitridation the As–N exchange is more pronounced and the GaN layer is thinner, effectively leading to even larger reduction of the QW barrier. The PL FWHM of both the nitridated and GaN-passivated sample are reduced by approximately 6 meV compared with the unpassivated QW.

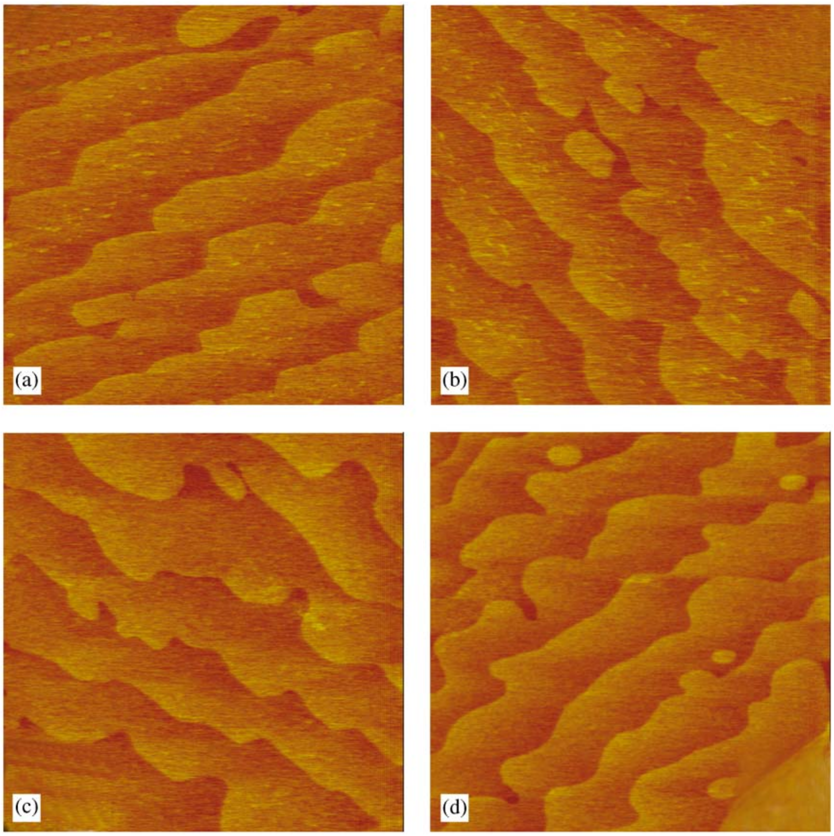

Fig. 3. AFM micrographs of (a) deep-QW, (b) unpassivated, (c) GaN-passivated, and (d) nitridation-passivated near-surface QW samples. No clear difference can be observed between (c) the epitaxial GaN layer and (d) the nitridated GaAs surface. The scan size is $3 \times 3\,\mu m^2$ and the vertical scale is 3 nm.

Fig. 3 shows the AFM micrographs of (a) a deep-QW, (b) unpassivated, (c) GaN-passivated, and (d) nitridation-passivated near-surface QW samples. The AFM scan size is $3 \times 3\,\mu m^2$ and the vertical scale is 3 nm. In Figs. 3(a) and (b), small 2D islands can be seen on the GaAs atomic layer terraces. These are presumably GaAs islands. In (c) and (d), no such small islands are seen. However, the surface morphologies are typical to 2D island growth with larger islands near the step edges. No clear difference can be observed between (c) the epitaxial GaN layer and (d) the nitridated GaAs surface. All in all, the passivation treatments do not seem to degrade the surface morphology of the sample.

The effect of the thickness of the GaN passivation layer on the PL of the near-surface quantum wells was studied by varying the growth time of GaN. Fig. 4 shows low-temperature PL spectra from 6 nm thick $In_{0.20}Ga_{0.80}As/GaAs$ near-surface QWs passivated with 1–3 MLs of GaN. The thickness of the GaAs cap is 5 nm. Blue shifts of 1.3 and 3.9 meV are observed as the nominal thickness of GaN is increased from 1 ML to 2 and 3 ML, respectively. This shows that a thicker GaN layer with the band gap larger than that of GaAs compensates the red shift seen in Fig. 2. The PL intensity is nearly the same for the samples with GaN thickness of 1 and 3 ML. For the sample with 2 ML of GaN, the PL intensity is approximately

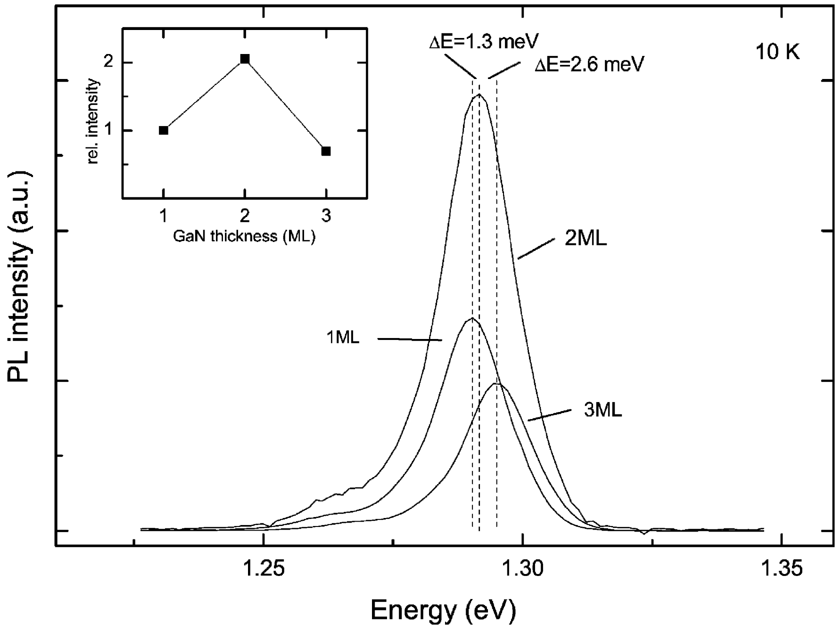

Fig. 4. PL spectra of passivated 6 nm thick $In_{0.20}Ga_{0.80}As/GaAs$ near-surface QWs with varying thickness of GaN. The inset shows the relative PL intensity as a function of the thickness of the GaN passivation layer.

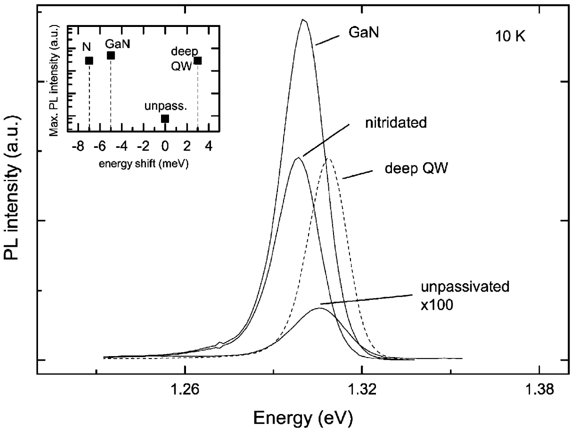

Fig. 5. PL spectra of passivated 4 nm thick $In_{0.25}Ga_{0.75}As/GaAs$ near-surface QWs after samples stored about 5 months in ambient air. The intensity of GaN-passivated sample is nearly three orders of magnitude larger compared with unpassivated sample.

two times higher. The surface morphologies of all three samples were alike (AFM micrographs not shown here).

PL measurements of 4 nm thick $In_{0.25}Ga_{0.75}As/GaAs$ near-surface QWs were carried out after storing the samples for about 5 months in ambient air. The spectra are shown in Fig. 5. The PL intensity of the GaN-passivated sample is nearly 10^3 times larger compared with the unpassivated QW. The intensities of nitridated, GaN-passivated, and deep-QW structures are in the same order of magnitude. The photoluminescence of InGaAs/GaAs deep QWs should not typically be affected by oxidation. This implies that nitridation and GaN passivation have protected the samples against degradation caused by oxidation. Overall, the PL intensity enhancement results show that both the epitaxial GaN and the nitridated GaAs passivate the GaAs surface and this effect lasts over time.

4. Conclusions

In summary, photoluminescence enhancement of $In_xGa_{1-x}As/GaAs$ near-surface QWs by epitaxial in situ GaN passivation is reported. The nitridation of surfaces using DMHy during post-growth cool-down is also shown to be an effective passivation method. The low-temperature PL measurements of near-surface QWs showed GaN passivation to enhance the intensity approximately by a factor of 20 compared with an unpassivated QW. For samples stored in ambient air for 5 months this factor was close to 10^3. A GaN layer thickness of 2 ML yielded the highest PL enhancement. The results suggest that the introduced ultra-thin epitaxial GaN layer grown on GaAs is an efficient in situ method for surface passivation.

References

[1] M. Losurdo, P. Capezzuto, G. Bruno, Appl. Phys. Lett. 81 (2002) 16–18.

[2] S. Anantathanasarn, H. Hasegawa, Appl. Surf. Sci. 190 (2002) 343–347.

[3] S. Anantathanasarn, S. Ootomo, T. Hashizume, H. Hasegawa, Appl. Surf. Sci. 159/160 (2000) 456–461.

[4] Y. Wada, K. Wada, Appl. Phys. Lett. 63 (1993) 379.

[5] Y. Wada, K. Wada, J. Vac. Sci. Technol. B 12 (1994) 3084.

[6] H. Lipsanen, M. Sopanen, M. Taskinen, J. Tulkki, J. Ahopelto, Appl. Phys. Lett. 68 (1996) 2216–2218.

[7] H. Yang, O. Brandt, A. Trampert, K.H. Ploog, Appl. Surf. Sci. 104/105 (1996) 461–467.

[8] J. Sormunen, J. Toivonen, M. Sopanen, H. Lipsanen, Appl. Surf. Sci. 222 (2004) 286–292.

[9] H. Sato, H. Takahashi, A. Watanabe, H. Ota, Appl. Phys. Lett. 68 (1996) 3617–3619.

[10] M.E. Heimbuch, A.L. Holmes Jr., C.M. Reaves, M.P. Mack, S.P. DenBaars, L.A. Coldren, J. Electron. Mater. 23 (1994).