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GaAs surface passivation by ultra-thin epitaxial GaP layer and surface As–P exchange

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Abstract

The GaAs surface passivation effects of epitaxially grown ultra-thin GaP layers and surface As–P exchange have been investigated. Optical properties of passivated and unpassivated InGaAs/GaAs near-surface quantum wells (QWs) grown by metal organic vapor phase epitaxy (MOVPE) are studied by low-temperature continuous-wave and time-resolved photoluminescence (PL). By optimizing the growth conditions, smooth surface morphologies and significant improvement of optical properties were observed for both passivation methods. Passivation improved the PL intensity more than two orders of magnitude and notably increased the PL decay time.

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1. Introduction

It is well known that the high density of surface states of GaAs may cause a large surface recombination velocity and Fermi level pinning near the middle of the band gap. These characteristics impose some limitations on optical and electrical performance of low-dimensional devices. Various in and ex situ surface passivation techniques using different material combinations and processing methods have been intensively investigated to reduce this effect. Chemical passivation with sulfur is one of the widely studied conventional passivation methods [1,2]. It has also been reported that epitaxial in situ passivation methods are more efficient than other passivation techniques. Significant passivation effects can be achieved by, e.g., metal organic vapor phase epitaxy (MOVPE) grown thin InP and GaN layers [3–6]. Surface As–P exchange treatment has also been studied widely for GaAs surface passivation [7–10]. By exposing GaAs surface to phosphine or tertiarybutylphosphine (TBP) at elevated temperature, a very thin layer of GaP is formed on the GaAs surface via As–P exchange. However, most of the previous

phosphorus passivation studies consider only surface As–P exchange while the passivation effects of epitaxially grown GaP are rarely reported.

In this paper, we study GaAs surface passivation by using both epitaxially grown ultra-thin GaP layers and surface As–P exchange. The passivation effects are characterized by studying low-temperature photoluminescence (PL) and time-resolved photoluminescence (TRPL) of the passivated and unpassivated MOVPE grown InGaAs/GaAs near-surface quantum wells (QWs). The growth conditions of GaP and surface phosphorization are investigated for optimum passivation effects. For both methods, the near-surface QWs show significantly enhanced PL intensity and longer PL decay times compared to those of the unpassivated samples.

2. Experimental

All near-surface QW and passivation layers were fabricated on semi-insulating GaAs (1 0 0) substrates in a horizontal MOVPE reactor at atmospheric pressure using trimethylindium (TMIn), trimethylgallium (TMGa), tertiarybutylarsine (TBAs) and TBP as precursors for indium, gallium, arsenic and phosphorus, respectively. The near-surface QW structure consists of a 100 nm thick GaAs buffer layer, a 4 nm thick

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$\text{In}_{0.22}\text{Ga}_{0.78}\text{As}/\text{GaAs}$ QW and a 5 nm thick GaAs cap layer. An unpassivated deep QW sample, with a 20 nm thick cap layer, was also grown for reference. All the near-surface QWs were grown at 650 °C and V/III ratios used for GaAs and InGaAs layers were 27 and 23, respectively. The temperatures mentioned in this report are thermocouple readings [11] and V/III ratios are molar flow ratios. Layer thickness and indium composition of the QW was determined by a high-resolution triple-axis X-ray diffractometer (HR-XRD).

Two kinds of passivation methods were utilized, epitaxially grown ultra-thin GaP layer and surface phosphorization. The growth temperature of the GaP passivation layer was varied between 550 and 640 °C while the V/III ratio was 130. At 580 °C, nominally 1 mono-layer (ML) thick GaP layers were grown with V/III ratios of 130, 200 and 300 to study the effect of V/III ratio. In order to study the effect of the passivation layer thickness, 1–3 MLs of GaP was deposited at 580 °C with a V/III ratio of 130. The surface phosphorization was realized by exposing the samples to TBP flows of 330, 500 and 730 $\mu\text{mol}/\text{min}$ during the cooling from 600 to 400 °C after the growth of the GaAs cap layer.

The low-temperature (10 K) continuous-wave PL measurements were conducted by utilizing a diode-pumped frequency-doubled Nd:YVO₄ laser emitting at 532 nm for excitation. A liquid-nitrogen-cooled germanium detector and standard lock-in techniques were used to record the PL spectra. The low-temperature TRPL measurements were performed by exciting

the samples with 150 fs pulses at 780 nm from a mode locked Ti:sapphire laser and by detecting the signal using a Peltier-cooled microchannel plate multiplier and time-correlated single photon counting electronics. The surface morphology of the samples was investigated by contact-mode atomic force microscopy (AFM).

3. Results and discussion

Fig. 1 shows the AFM images of GaP-passivated (1 ML thick, grown at 620 and 580 °C), surface phosphorized and unpassivated near-surface QW samples. Small islands, possibly Ga droplets, were found on the GaP-passivated sample surfaces if the passivation layers were grown at temperatures above 600 °C (Fig. 1(a)). The main reason for the three-dimensional morphology in these samples might be the arsenic to phosphorus exchange and arsenic desorption at higher temperatures [12]. Smooth sample surfaces and clear atomic layer terraces are observed from the GaP-passivated samples if the passivation layers are grown at temperature below 600 °C (Fig. 1(b)) as well as from the phosphorized sample (Fig. 1(c)). Comparison with the unpassivated sample (Fig. 1(d)) indicates that the passivation layer does not degrade the surface morphology of the samples.

Fig. 2 shows the normalized maximum low-temperature PL intensity of the 1 ML thick GaP-passivated samples as a function of the growth temperature of the passivation layer. All

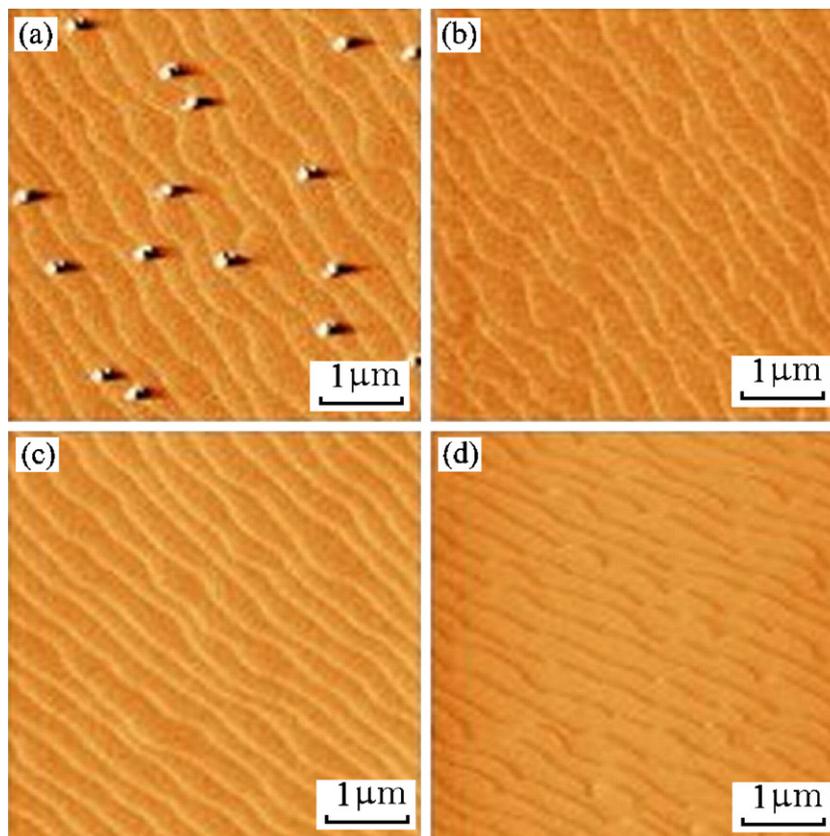


Fig. 1. AFM images of near-surface QW samples: (a) GaP-passivated at 620 °C, (b) GaP-passivated at 580 °C, (c) surface phosphorized and (d) unpassivated. The scan size is 5 $\mu\text{m} \times 5 \mu\text{m}$ and the vertical scale is 5 nm.

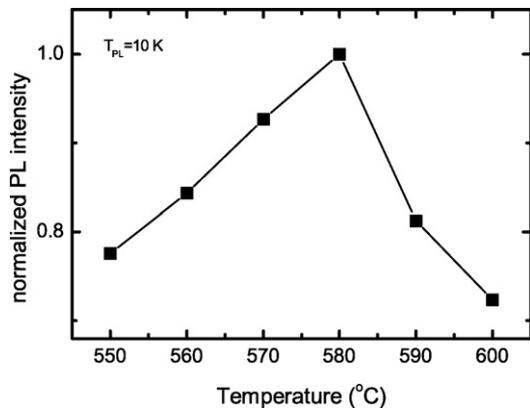


Fig. 2. Normalized maximum low-temperature PL intensity of a 1 ML thick GaP-passivated near-surface QW as a function of the growth temperature of the GaP layer.

the samples were measured with the excitation intensity of 10 W/cm^{-2} . Although all these samples show smooth surface morphologies in the AFM scans, the maximum PL intensity is obtained when the passivation layer was grown at $580 \text{ }^\circ\text{C}$. However, small fluctuations in the thickness of the GaAs cap or in the homogeneity of the QW could affect the PL intensity. In this case, the result of Fig. 2 indicates that the optimum growth temperature of thin GaP layer for passivation purpose is found between 560 and $590 \text{ }^\circ\text{C}$. According to PL results from Fig. 2 and AFM results from Fig. 1, the growth temperature for subsequent GaP passivation layers was chosen to be $580 \text{ }^\circ\text{C}$. In order to study the effect of V/III ratio, 1 ML thick GaP passivation layers were grown at V/III ratios of 130, 200 and 300. Comparison of the PL spectra of these samples (Fig. 3 (a)) shows that the effect of V/III ratio is not very remarkable. However, the best passivation effects were achieved at the V/III ratio of 130. The PL spectra of samples with different GaP passivation layer thicknesses, which were grown with a V/III ratio of 130, are shown in Fig. 3(b). The PL intensity seems to decrease slightly when the passivation layer thickness is increased. This may be caused by the increased strain between the GaP layer and GaAs substrate [12]. The passivation effect of surface phosphorization showed no obvious dependence on the TBP flow for flows larger than $300 \text{ } \mu\text{mol/min}$ (PL spectra not shown here).

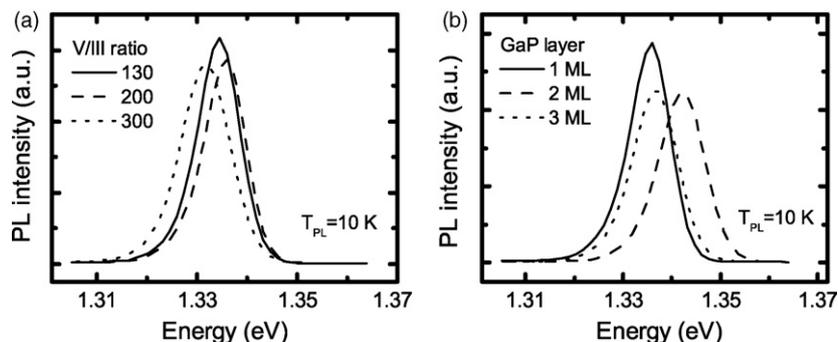


Fig. 3. (a) Low-temperature PL spectra of GaP-passivated near-surface QWs with various V/III ratios for the GaP layer. (b) Low-temperature PL spectra of GaP-passivated near-surface QWs with various GaP thicknesses.

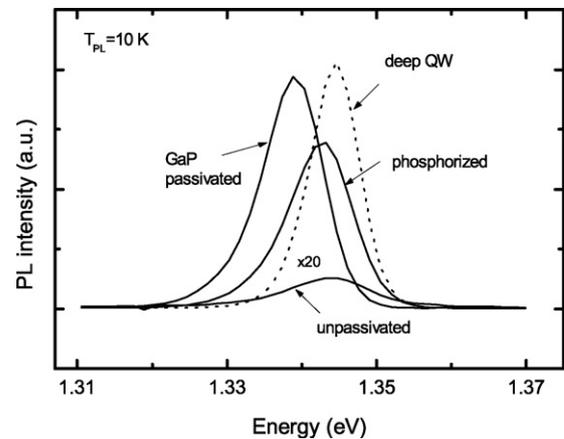


Fig. 4. Low-temperature PL intensities of GaP-passivated, surface phosphorized and unpassivated deep and near-surface QW samples.

Table 1

The relative intensity and full-width at half-maximum of the PL spectra shown in Fig. 4

Sample	PL intensity	FWHM (meV)
Unpassivated	1	26.2
Deep QW	161	15.9
GaP-passivated	152	19.7
Phosphorized	109	20.9

The PL intensity of the unpassivated near-surface QW has been normalized to 1.

Fig. 4 shows the low-temperature PL spectra of the best samples from previous series. In these samples, a 1 ML thick GaP passivation layer was grown with the V/III ratio of 130 and surface phosphorization was carried out at the TBP flow of $330 \text{ } \mu\text{mol/min}$. The PL intensity of the deep QW sample (dot line) is also shown as a reference. Table 1 shows the relative PL intensity and full-width at half-maximum (FWHM) of the PL spectra in Fig. 4. From Table 1 one can see that the PL intensity was improved over two orders of magnitude by both passivation methods and becomes comparable to that of the deep QW. However, the sample which was passivated by an epitaxial GaP layer shows higher PL intensity than the surface phosphorized sample. At the same time, GaP passivation and surface phosphorization resulted in a small PL red shift, with respect to the unpassivated QW PL peak energy, of 5.8 and 1.5 meV ,

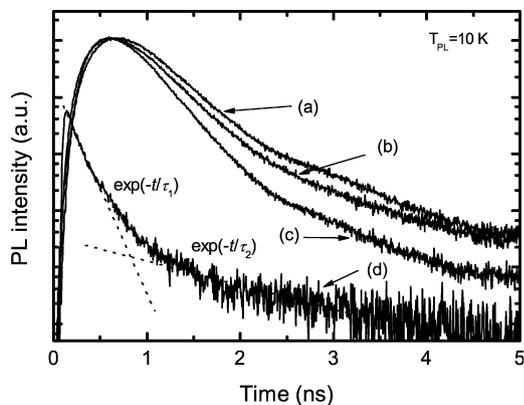


Fig. 5. Low-temperature TRPL transients of: (a) surface phosphorized, (b) GaP-passivated, (c) deep QW and (d) unpassivated near-surface QW samples.

Table 2
PL decay times of passivated and unpassivated near-surface QW

Sample	τ_1 (ns)	τ_2 (ns)
Unpassivated	0.36	2.2
Deep QW	0.43	2.3
GaP-passivated	0.51	2.6
Phosphorized	0.57	2.5

respectively. We assume that this energy shift might be caused by the growth nonuniformity of the QWs in different growth runs.

TRPL measurements were also used to characterize the passivation effects. Fig. 5 shows the low-temperature TRPL transients of the passivated and unpassivated samples at the wavelength of the maximum continuous-wave PL intensity. The background signal has been subtracted from the data. In all the samples, the PL transients over time exhibit double-exponential decay. This may be related to the band-bending caused by surface states [13,14] or exciton transfer between the continuum (free carriers) and the bound states [15]. The PL decay times τ_1 and τ_2 were determined by using the second order exponential fit

$$y(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

as indicated in Fig. 5. The decay time τ_i can be expressed as $\tau_i^{-1} = \tau_{R,i}^{-1} + \tau_{NR,i}^{-1}$, where $\tau_{R,i}^{-1}$ and $\tau_{NR,i}^{-1}$ are the radiative and non-radiative decay times, respectively. Good agreement between the fit and the data was achieved for all the samples. The obtained values of τ_1 and τ_2 are shown in Table 2. It can be

clearly seen that in both passivated samples the decay time τ_1 was notably increased while τ_2 was almost unchanged.

4. Conclusion

In conclusion, GaAs surface passivation effects of in situ epitaxially grown ultra-thin GaP layers and surface As–P exchange have been investigated. Optical properties of passivated and unpassivated $\text{In}_{0.22}\text{Ga}_{0.78}\text{As}/\text{GaAs}$ near-surface quantum wells were characterized by PL and TRPL measurements to study the passivation effects. The growth conditions of the passivation layers were optimized by changing the growth temperature, V/III ratio and layer thickness. The best result for GaP passivation was obtained when a 1 ML thick epitaxial GaP layer was grown at the temperature of 580 °C with the V/III ratio of 130. Surface As–P exchange was performed by exposing the sample surface to a TBP flow during cooling from 600 to 400 °C after the growth of the cap GaAs layer. The passivation effect of surface phosphorization showed no obvious dependence on the TBP flow for flows larger than 300 $\mu\text{mol}/\text{min}$. Both passivation methods improved the PL intensity and increased the PL decay time compared to those of unpassivated samples.

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