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Growth and surface passivation of near-surface InGaAs quantum wells on GaAs (1 1 0)

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Abstract

The growth and surface passivation of near-surface InGaAs quantum wells (QWs) on GaAs (1 1 0) substrate have been investigated. Triangular shaped small islands, approximate areal density of 10^7 cm^{-2} , are observed on metal organic vapor phase epitaxially grown GaAs single layer and InGaAs multi-quantum wells (MQWs) surfaces in a wide range of growth temperatures. By optimizing the growth conditions, high quality $\text{In}_{0.22}\text{Ga}_{0.78}\text{As}$ QWs with optical properties comparable to the same structure grown on GaAs (1 0 0) are obtained. Near-surface single QWs are used to study the surface passivation. Epitaxially *in situ* grown mono-layer thick GaP and InP layers as well as surface phosphorization with tertiarybutylphosphine (TBP) are utilized as passivation methods. Passivation significantly increases photoluminescence (PL) intensity and carrier lifetime of near-surface QWs. The best passivation efficiency is obtained by surface phosphorization with TBP on (1 1 0)-oriented near-surface QW while the ultra-thin InP layer is the best on (1 0 0)-oriented near-surface QW. After 7 months of air exposure, all passivated near-surface QWs still show high PL intensity comparable to deep QW while the PL intensity of unpassivated samples degraded severely. Also, the differences between the optical properties of QWs on GaAs (1 1 0) and (1 0 0) substrates are observed and discussed.

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1. Introduction

GaAs (1 1 0) orientation is more favorable than GaAs (1 0 0) in some applications due to its high impact ionization efficiency [1] in optical devices and preference in epitaxial growth of zincblende-on-diamond system [2]. (1 1 0)-Oriented AlGaAs quantum wells (QWs) were also found to be particularly suitable for spintronic application due to their long carrier relaxation times [3]. Epitaxial growth of bulk [4–6] and QW [7,8] structures on GaAs (1 1 0) substrates by molecular beam epitaxy (MBE) has been reported in detail before. In all these studies the surface structure was found to be faceted with triangular

shaped islands having surface densities of approximately 10^6 cm^{-2} [6]. However, growth of (1 1 0)-oriented GaAs and QWs has not been widely studied by using metal organic vapor phase epitaxy (MOVPE).

In addition, various GaAs surface passivation techniques have been intensively studied due to the high density of surface states which can bring some serious limitations to the material and device performance. QW lasers grown on GaAs (1 0 0) substrates have (1 1 0)-oriented mirrors. Destruction of laser mirror surfaces due to the overheating caused by optical absorption on the surface states is the most significant factor limiting the power density of high-power laser [9,10]. Better passivation methods for (1 1 0) surfaces could provide improved laser performance. The *in situ* epitaxial passivation is considered to be a more efficient method than the other techniques [11–14] on the

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surface passivation of GaAs (100). However, the epitaxial passivation methods of GaAs (110) surface are rarely reported.

In this paper, we study MOVPE growth and surface passivation characteristics of near-surface InGaAs QWs on GaAs (110) substrates. GaAs single layer and InGaAs multi-quantum wells (MQWs) are used to study the surface morphologies and structural properties. High quality QW structures were grown on the GaAs (110) substrate and significant passivation effects were obtained by using *in situ* grown ultra-thin passivation layers. Different passivation methods show different passivation efficiency on (110) and (100)-oriented near-surface QWs. All passivated samples show good time stability after long time air exposure.

2. Experimental procedure

All the samples were grown on GaAs (110) 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. GaAs single layers with 10, 50, and 100 nm thicknesses and $\text{In}_x\text{Ga}_{1-x}\text{As}$ MQWs were grown for studying the surface morphology and structural quality. The five-period MQW structure consists of 4 nm thick InGaAs QWs and 20 nm thick GaAs barriers grown on top of a 100 nm thick GaAs buffer layer. The growth temperature of GaAs single layer is 650 °C, and it was varied in the range of 600–720 °C for the MQW growth while the V/III ratio was 23. The temperatures mentioned in this report are thermocouple readings [15] and V/III ratios are molar flow ratios. There was also a (100) GaAs substrate, in addition to the (110) substrate, in the reactor in each growth run for reference.

The passivation effects were studied by investigating the optical properties of a near-surface single QW structure consisting of a 4 nm thick $\text{In}_{0.22}\text{Ga}_{0.78}\text{As}/\text{GaAs}$ QW and a 5 nm thick GaAs cap layer. An unpassivated deep QW sample, with a 20 nm thick cap layer, was grown for

reference. Three kinds of *in situ* passivation methods were utilized. Nominally 1 ML thick GaP and InP passivation layers were grown on top of the cap layer at a temperature of 580 and 650 °C with a V/III ratio of 130 and 230, respectively. The surface phosphorization was realized by exposing the sample surface to a TBP flow of 330 $\mu\text{mol}/\text{min}$ during the cooling from 600 to 400 °C after the growth of the GaAs cap layer. All the passivated and unpassivated near-surface QW structures were also grown in the same growth run on GaAs (100) substrates for comparison.

A contact-mode atomic force microscope (AFM) was used to investigate sample surface morphology. Layer thickness and indium composition of the QW were determined by a high-resolution X-ray diffractometer (HR-XRD). 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 time-resolved photoluminescence (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.

3. Results and discussion

3.1. Growth of QWs on GaAs (110) substrate

Surface morphology and the structural quality of GaAs single layers and $\text{In}_x\text{Ga}_{1-x}\text{As}$ MQWs grown on GaAs (110) substrate were studied. Triangular shaped small islands were observed on the surfaces of the GaAs epilayers. Fig. 1 shows the AFM images of GaAs layers (grown at 650 °C) with the thickness of 10 and 100 nm. The average base size and average height of a typical island are 100 and 1–2 nm, respectively. The approximate density of

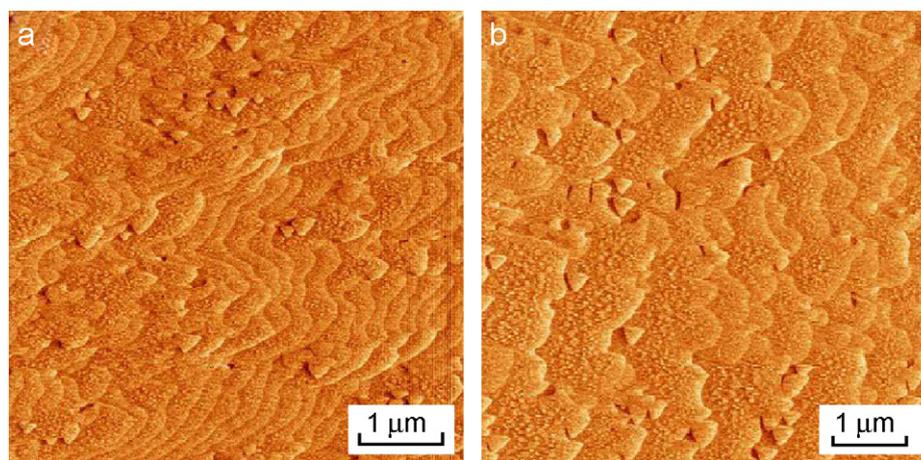


Fig. 1. Surface AFM images of GaAs layers (grown at 650 °C) on GaAs (110) substrate with the thickness of (a) $d = 10$ nm and (b) $d = 100$ nm. The scan size is $5 \times 5 \mu\text{m}^2$ and the vertical scale is 5 nm.

the islands is 10^7 cm^{-2} when the GaAs layer thickness is 10 nm. Changing the thickness of the GaAs layer from 10 to 100 nm results in a slight decrease in island density. Similar morphologies were also observed on MQW surfaces. Variation of the growth temperature and V/III ratios of MQWs did not have significant effect on the shape and size of the islands (AFM images not shown), but the density of islands decreased slightly compared to that of on the GaAs epilayer. Based on these results, we assume that the island characteristics of the epilayers are caused by the original facet-structured surface of the GaAs (110) substrate. The explanation for the formation of such island structure on GaAs (110) surface has been discussed in Refs. [5,6,16] in detail. The bonding of the Ga and As atoms naturally exposes both types of (111) plane on the (110)-oriented GaAs surface. Kinetic studies have shown that the incoming As atoms are strongly attracted to the stable (111) Ga surface and will bond on there faster than Ga atoms bond on the (111) As surface [5]. These chemisorbed atoms will then provide a basis for further chemisorption of the incoming Ga and As atoms. As a result, a facet begins to form from the fast growing (111) Ga surface with sides of (100) and (010) filling in and thus creating the facet shape, and, consequently, resulting in a triangular shaped island.

Fig. 2 shows the (022) HR-XRD omega-2theta curve of an MQW sample grown at 650°C on a GaAs (110) substrate. The inset shows the room temperature PL spectrum of the same sample. The simulated indium composition (0.22) and QW thickness (3.9 nm) are in good agreement with the expected values (0.25 and 4.0 nm) based on the growth parameters. A quite similar correlation was achieved also for all the other MQW samples grown at different temperatures. Almost the same parameter values were obtained from the same MQW structure on GaAs (100) and (110) substrates. Apart from the island-related characteristics of (110) surfaces, the structural and optical

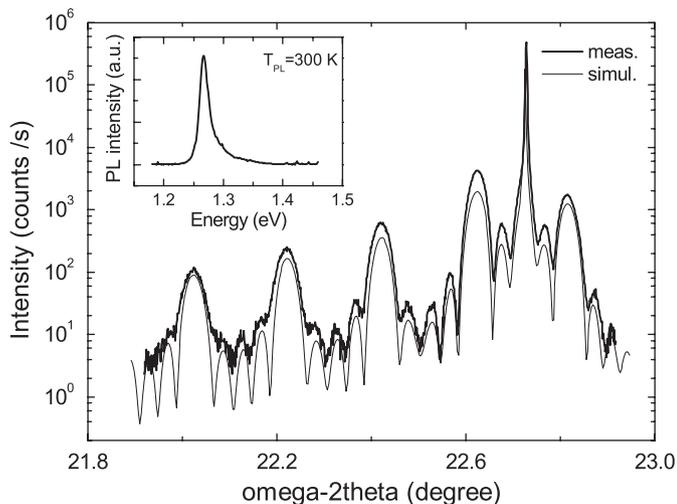


Fig. 2. Measured and simulated (022) HR-XRD omega-2theta curves of an MQW sample grown at 650°C on GaAs (110) substrate. The inset shows the room temperature PL spectrum of the same sample.

quality of the InGaAs MQWs grown on a GaAs (110) substrate were similar to those grown on a GaAs (100) substrate. This indicates that similar high quality QWs can be obtained by MOVPE fabrication using the same growth conditions on both (110) and (100) GaAs substrates.

3.2. GaAs (110) surface passivation

Near-surface $\text{In}_{0.22}\text{Ga}_{0.78}\text{As}$ single QWs were grown at 650°C for the study of subsequent surface passivation. The structures of the samples for the passivation study are described in the experimental section. The AFM images of the unpassivated and passivated near-surface QW samples are shown in Fig. 3(a)–(d). The small islands can still be seen on the both unpassivated and passivated (110) QW sample surfaces. The ultra-thin passivation layers did not significantly affect the surface morphology of the samples. On the other hand, the clear atomic layer terraces were observed on the unpassivated and passivated (100) QW sample surfaces (Fig. 3(e) and (f)).

Fig. 4 shows the low-temperature PL spectra of the passivated and unpassivated near-surface QW samples on GaAs (110) substrates. The PL spectrum of the deep QW sample is also shown as a reference (dot line). The low-temperature TRPL transients of the unpassivated and surface phosphorized samples taken at the wavelength of the maximum continuous-wave PL intensity are shown in the inset (the TRPL transients from the other samples are not shown). In all the samples, the TRPL transients over time exhibit double-exponential decay. This behavior may be related to the band-bending caused by surface states [17,18] or exciton transfer between the continuum (free carriers) and the bound states [19]. The PL decay times τ_1 and τ_2 were determined by using the second-order exponential fit

$$y(t) = C + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

as indicated in Fig. 5(a). 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. This model agreed well with the experimental data. The relative PL intensity, full-width at half-maximum (FWHM), and PL decay times τ_1 , τ_2 of all the passivated and unpassivated samples on both GaAs (110) and (100) substrates are listed in Table 1.

From Fig. 4 and Table 1, it can be clearly seen that the PL intensity of the near-surface QW is significantly increased by all the passivation methods. The enhancement of the PL intensity by passivation is up to two orders of magnitude. However, different passivation methods show different passivation efficiency depending on the substrate orientation. The largest PL enhancement on (110)-oriented near-surface QW is obtained by surface phosphorization with TBP while the ultra-thin InP layer passivation is the best on (100)-oriented near-surface QW. The GaP-passivated QW shows comparable PL intensity to the surface phosphorized one on the (110)

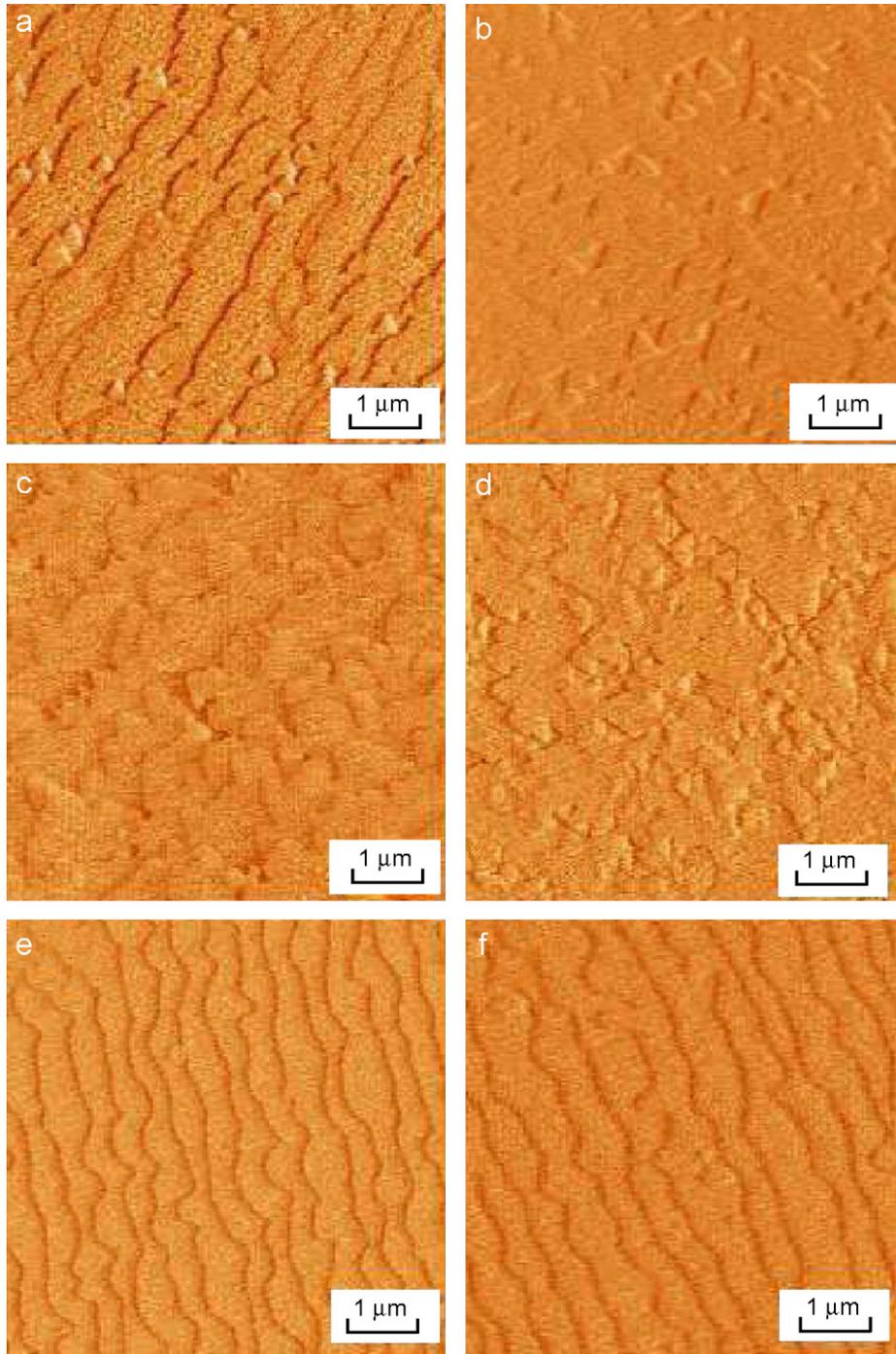


Fig. 3. AFM images of (a) unpassivated, (b) GaP-passivated, (c) surface phosphorized, and (d) InP-passivated near-surface QW samples on a GaAs (110) substrate. AFM images of (e) unpassivated and (f) InP-passivated near-surface QW reference samples on GaAs (100) substrate. The scan size is $5 \times 5 \mu\text{m}^2$ and the vertical scale is 5 nm.

substrate, but the enhancement of PL intensity on GaAs (100) substrate is relatively lower. The FWHM values for the passivated samples are a little lower compared to the unpassivated sample on both substrates, but the (100) QWs show generally smaller FWHM values than their (110) counterparts.

The TRPL results show that the PL decay time τ_1 is increased notably in all the passivated samples while τ_2 remains almost unchanged. The increase of τ_1 in the

passivated samples can be attributed to the decrease of the non-radiative recombination in the early stage of the decay [20,21] due to the passivation effect. However, the values of τ_1 in (110) QWs are a little higher than those of (100) QWs, i.e., $(\tau_1)_{110} > (\tau_1)_{100}$ (Fig. 5). It indicates that the ultra-thin passivation layers can efficiently reduce the surface states of the near-surface QWs and it is more efficient on (110) QWs than on (100) QWs. In the later stage of the decay, the radiative recombination dominates

the decay process while the non-radiative recombination caused by the surface states has less effect. According to this assumption, the values of τ_2 in both passivated and unpassivated samples should be the same. But the value of τ_2 in (110) near-surface QWs seems to be somewhat lower than that in (100) QWs, $(\tau_2)_{110} \lesssim (\tau_2)_{100}$.

The time stability of the passivation effect was studied by measuring low-temperature PL intensities of the same samples after the samples were stored in air ambient for 7 months. The PL measurement setup and all the parameters were the same as in the previous measurement. Comparison of the maximum PL intensity of the passivated and unpassivated (110) and (100) QWs are shown in Fig. 6. It can be clearly seen that the PL intensity of all the samples were degraded over time, but all the passivated samples still show quite high, more than three orders of magnitude larger PL intensity than the unpassivated samples on both

substrates after extended air exposure. It implies that the passivation effect also protects the samples against oxidation in addition to reducing the density of surface states while the unpassivated samples degrade severely. The PL intensity of all the passivated samples degraded approximately 20–40%, comparable to the deep QW. However, the degradation of the PL intensity of the unpassivated QWs (85% for the (110) substrate and 91% for the (100) substrate, respectively) is significantly higher compared to the passivated samples and the degradation is faster on the (100) substrate.

According to the comparison of the optical properties (Table 1 and Fig. 6), the QWs grown on differently oriented GaAs substrates behave differently besides the passivation effects. These overall differences, observed in this work, of GaAs (110) and (100) substrates are listed in Table 2. We assume that all of these differences were

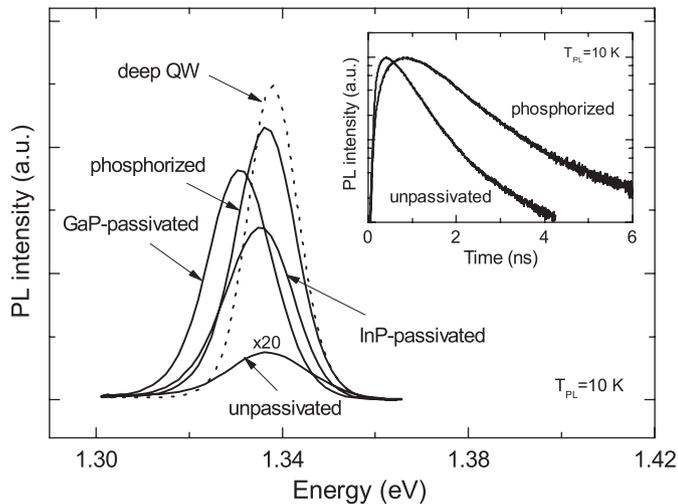


Fig. 4. Low-temperature PL spectra of the passivated and unpassivated near-surface QWs on GaAs (110) substrate. The inset shows the TRPL transients of the unpassivated and surface phosphorized samples.

Table 1

Key characteristics of PL and TRPL measurement results for various passivated near-surface QWs on GaAs (110) and GaAs (100) substrates

Sample	PL intensity	FWHM (meV)	τ_1 (ns)	τ_2 (ns)
110				
Unpassivated	1	24.9	0.46	2.1
Deep QW	132	14.2	0.69	2.3
GaP-passivated	96	18.5	0.81	2.2
Phosphorized	115	17.2	0.86	2.4
InP-passivated	72	19.4	0.77	2.2
100				
Unpassivated	1	16.2	0.33	2.7
Deep QW	162	10.3	0.51	2.8
GaP-passivated	101	10.6	0.56	2.7
Phosphorized	123	10.7	0.69	2.9
InP-passivated	135	13.6	0.63	2.8

The PL intensity of the unpassivated near-surface QWs have been normalized to 1.

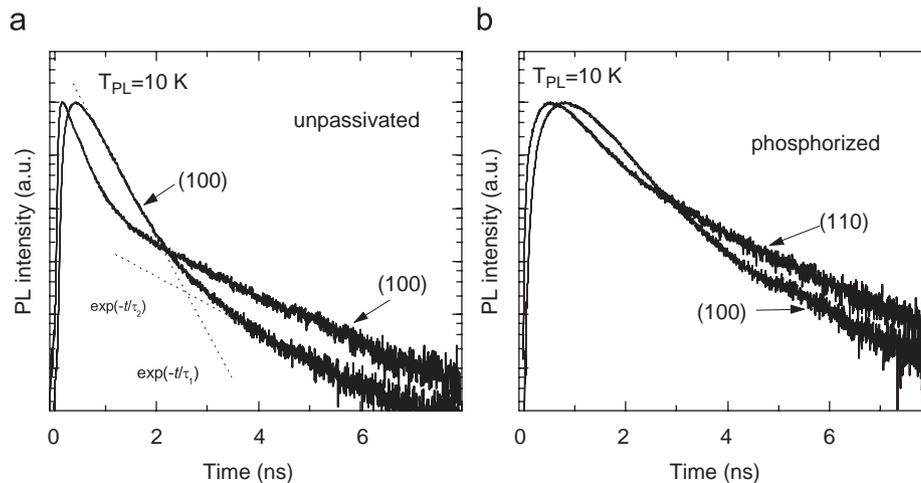


Fig. 5. Comparison of low-temperature TRPL transients of (a) unpassivated and (b) surface phosphorized near-surface QW on GaAs (110) and (100) substrates.

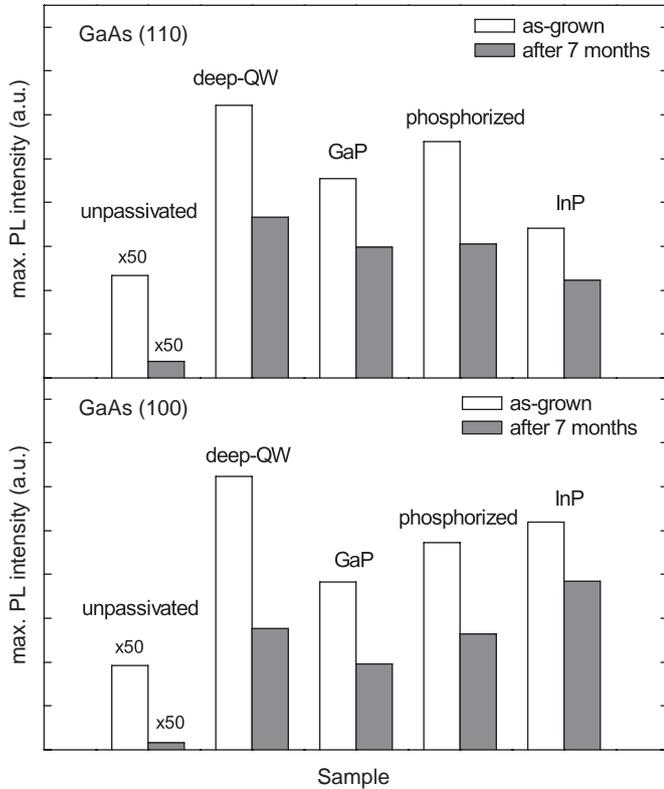


Fig. 6. Comparison of the maximum low-temperature PL intensity of as-grown and 7 months air exposed passivated and unpassivated QWs on both GaAs (110) and (100) substrates. For clarity, the PL intensity of unpassivated samples is multiplied by a factor of 50.

Table 2

The overall differences of optical properties of QW structure on GaAs (110) and (100) substrates

PL peak	$(FWHM)_{110} > (FWHM)_{100}$
PL intensity degradation	$(\gamma)_{110} < (\gamma)_{100}$
TRPL transient	$(\tau_1)_{110} > (\tau_1)_{100}$ $(\tau_2)_{110} < (\tau_2)_{100}$

caused by the different physical properties of the GaAs substrates. On GaAs (100) substrate, the more severe degradation of the PL intensity and the smaller PL decay time at the early stage of the decay τ_1 indicate that the density of surface states and non-radiative recombination centers is generally higher compared to (110)-oriented GaAs. The smaller values of τ_2 in GaAs (100) maybe related to the larger surface energy band-bending [22] due to the surface lattice relaxation [22,23] on the (110)-oriented epilayer. As for the broader PL emission (larger FWHM) from the (110) QWs, we assume it was caused by the fluctuation of indium composition of the InGaAs layer due to the island formation.

4. Conclusion

In summary, the growth and surface passivation of near-surface InGaAs QWs on GaAs (110) substrates, by

MOVPE, were investigated. The surface passivation effects were characterized by studying the optical properties of *in situ* passivated near-surface $\text{In}_{0.22}\text{Ga}_{0.78}\text{As}$ QWs. Epitaxially grown ultra-thin GaP and InP layers and surface phosphorization with TBP were utilized as passivation. The following results were obtained: (i) triangular shaped small islands, approximate density of 10^7 cm^{-2} , were observed on both GaAs and MQWs surfaces in a wide range of growth temperature. (ii) All passivation methods significantly increased the PL intensity and carrier lifetime of the near-surface QWs. However, the different passivation methods showed different passivation efficiency on (110) and (100)-oriented near-surface QWs. The largest PL enhancement on (110)-oriented near-surface QW was obtained by surface phosphorization with TBP while the ultra-thin InP layer passivation was the best on (100)-oriented near-surface QW. (iii) Optical properties of QWs grown on GaAs (110) and (100) substrates behave differently in some aspects, such as width of PL peaks, degradation of PL intensity over time and PL decay time at different decay stages. We assume all of these differences are mainly caused by the original physical properties of different oriented GaAs substrate.

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