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Interlayer formation due to group V-hydride stabilization during interruptions of MOVPE growth of InGaP

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Abstract

The effect of indium and arsenic carry-over and of arsenic–phosphorus exchange on unintentional interlayer formation due to prolonged stabilization under arsine or phosphine during InGaP growth interruptions in metalorganic vapour phase epitaxy (MOVPE) at 580 °C is investigated. Photoluminescence, x-ray diffraction, secondary ion mass spectrometry, transmission electron microscopy and capacitance–voltage (C–V) depth profiling of the electron concentration are used to detect and to characterize possible unintentionally formed interlayers. The C–V measurements show that purging with PH_3 mainly enhances the degree of ordering of an interlayer region due to a P-rich reconstruction of the InGaP surface during the growth interruption. The interlayer stress and band offset are too small to be detected by x-ray diffraction or photoluminescence. In contrast, purging with AsH_3 during InGaP growth interruption leads to strong arsenic incorporation, but does not lead to any change in the In concentration. The As-rich interlayer gives rise to additional photoluminescence peaks and compressive strain. The relatively large interlayer thickness detected by C–V and SIMS measurements of up to 20 nm indicates that arsenic accumulated during the prolonged growth interruptions carries over into the InGaP layer grown after the interruption. It is shown that the chosen growth conditions suppress the In carry-over, but As carry-over occurs additionally to the As–P exchange.

1. Introduction

Heterointerfaces between different semiconductors are the basis of band-gap engineering used for electronic and optoelectronic devices. However, the optimization of these interfaces is a challenge, especially, when switching between AsH_3 and PH_3 for the growth of (In, Ga)(As, P) layer structures. Unintentional interlayer formation during metalorganic vapour phase epitaxy (MOVPE) of InGaP-on-GaAs and GaAs-on-InGaP structures has often been reported [1–5]. Such interlayers can dramatically change the electrical and optical properties of device structures, such as heterobipolar transistors or laser diodes [6, 7]. For example, a growth interruption for switching from PH_3 flux to AsH_3 flux usually precedes the deposition of GaAs on top of InGaP. Depending on the growth temperature, on the time of purging with group-V hydrides and on their concentration during growth interruption, the formation of an interfacial layer can be modified. The intermediate layer formed at the

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InGaP-on-GaAs interface is usually less pronounced compared with the GaAs-on-InGaP system [2, 3]. In contrast to the InP-on-InGaAs system [8], it is limited to the uppermost layer, because, besides the As by P exchange forming a GaAsP interlayer, no P carry-over occurs [9]. The reason for that is the higher incorporation efficiency of arsenic from AsH_3 in comparison with phosphorus from PH_3 [10]. For GaAs-on-InGaP interfaces, several studies discuss, besides the P by As exchange, the influence of indium carry-over, caused by the known In-segregation effect or by an In-accumulation from parasitic In-deposits in the reactor chamber during the growth interruption, on the formation of an unintentional interlayer [1–3]. Such interlayers often give rise to an additional low temperature photoluminescence (PL) peak around 1.4 eV [1–5], which can be avoided by depositing additional interlayers [1, 2, 5] or by optimized gas switching/purging sequences [10]. The exchange of As by P has been carefully studied by *in situ* reflection anisotropy spectroscopy and x-ray diffraction during PH_3-stabilized interruptions of GaAs MOVPE growth [9].

Here, the interlayer formation as a result of P by As exchange during prolonged AsH_3-stabilized interruptions of InGaP MOVPE growth is studied at low growth temperature and hydride flows, which are known from our previous work to suppress the effect of indium carry-over when switching from InGaP to GaAs growth [11, 12]. To show that the effect of indium carry-over on interlayer formation is really suppressed, we characterize, in addition, the interfaces formed during prolonged PH_3-stabilized interruptions of the InGaP MOVPE growth. Because sheet charges occur at heterointerfaces with ordered InGaP layers due to polarization [12], we perform capacitance–voltage (C–V) studies with metal-semiconductor contacts on isotype heterojunctions, which are known to provide reliable values for the band offset in the presence of interfacial charges [11, 12]. We apply the C–V technique in addition to PL measurements in order to identify the inadvertent interlayers originating from growth interruptions by their conduction band offsets with respect to InGaP.

2. Experimental procedure

The InGaP and GaAs layers were grown in a horizontal MOVPE reactor (Aix 200) at 70 hPa using TMGa, TMIn, Si_2H_6, AsH_3 and PH_3 as precursors. InGaP alloy was grown at 580 °C on n-type (001) GaAs. A V/III input ratio of 70 and a growth rate of 2.5 μm h^{-1} were used. The InGaP layer growth was interrupted several times by switching-off the TMGa and TMIn flows for 60 s. During the growth interruption, the hydride flow was 75 sccm PH_3 or 10 sccm AsH_3 in 7 slm total hydrogen flow. InGaP growth was restarted by replacing the AsH_3 directly by PH_3 for 0.5 s and then switching-on the TMGa and TMIn flows at the same time. Thickness and composition of the InGaP layer as well as the strain of the interlayers were determined by high resolution x-ray diffraction at the (004) reflection. The lattice mismatch of the InGaP layer was smaller than 5×10^{-4}. The 514.5 nm line of a cw Ar^+ laser was used to excite low-temperature PL. In order to determine the electronic properties of the interfaces by the C–V method, the layer structures were Si-doped with carrier concentrations in the 10^{17} cm^{-3} range (cf [13]). The C–V technique allows us to investigate depth profiles of the electron concentration *n*. For the investigated structures, the experimental *n* versus depth profiles were compared with simulations using a programme of Snider *et al* [14], which self-consistently solves the coupled Schrödinger and Poisson equations. It is well known that C–V measurements on heterointerfaces independently provide values for the carrier concentration, the band offset, the position of the interface and the density of possible sheet charges [15, 16]. In all accompanying simulations, additional charges due to polarization or deep levels at the interfaces were not taken into account. The As, In, Ga and P concentrations were measured by secondary ion mass spectrometry (SIMS) with a depth resolution of 3.2 nm determined by the sputter rate. The interfaces were additionally investigated by transmission electron microscopy (TEM) using cross-sectional (002) dark field images taken at a magnification of 300 000 and an acceleration voltage of 400 kV.

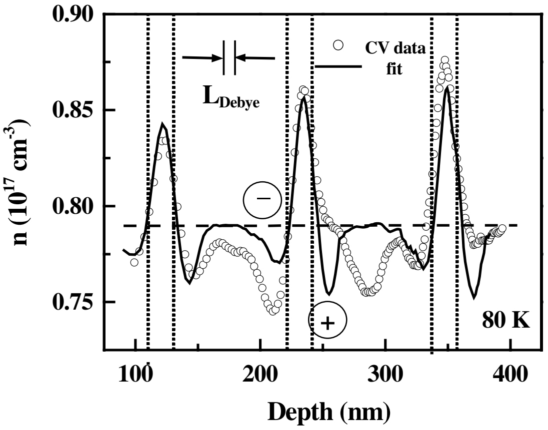

Figure 1. C–V depth profile of the electron concentration *n* measured at 80 K and 1 MHz for an InGaP layer deposited at 580 °C with three growth interruptions of 60 s under PH_3 flux (circles). Solid line—simulated fit, horizontal dashed line—doping level in InGaP and vertical dotted lines—interface positions of the interlayers according to the simulation.

3. Results

3.1. InGaP growth interruption under PH_3 stabilization

To study the impact of the stabilizing PH_3 flow on possible interfacial layer formation, the InGaP growth at 580 °C and low V/III ratio was interrupted several times for 60 s under PH_3. In the C–V depth profile of the electron concentration *n* shown in figure 1, clear peaks are visible at the interrupt positions with depleted regions on both sides. These features are characteristic of the presence of quantum wells (QWs). An unintentional interlayer is apparently formed during or after the growth interruptions. Detailed information on the interlayer is gained by comparison of the measured electron distribution with calculated depth profiles (see figure 1).

The measured electron distribution can be reasonably fitted by the model calculations using the approach given in [14] (cf the line in figure 1). Since the regions around the interfaces created by the growth interruptions have the same average carrier concentration like the bulk (horizontal dashed line), no additional charges have to be assumed for the fit. Local differences between data and simulation occur inside the InGaP layer and are due to polarization charges in the weakly ordered material [12, 17]. For the QW at the position of about 230 nm depth, it is especially seen that positive and negative polarization charges occur at the interlayer-on-InGaP and InGaP-on-interlayer interfaces, respectively (see the circles in figure 1). This indicates that, with respect to the InGaP layer, the degree of CuPt$_B$-type ordering is obviously changed inside the interlayer. In particular, we can conclude a higher degree of ordering for the interlayer formed during/after the growth interruption under PH$_3$ in InGaP [17]. The higher ordering degree of the interlayer may be the result of P-rich (2 × 1) reconstruction of the InGaP surface formed during the prolonged growth interruption at this low growth temperature due to the reduced phosphorus desorption. It is known that phosphorus dimers in the (2 × 1) symmetry at the growth surface support the bulk ordering of InGaP by creating strain in the layers just below the surface over up to four InGaP layers [18]. The occupation of certain lattice sites by diffusion of Ga and In to their energetically preferred lattice sites in the third subsurface atomic layer is biased by their different covalent radii. InGaP growth after the interruption takes place under low phosphorus flow, and the phosphorus-rich surface changes to more group-III rich conditions during further growth, leading to more (2 × 4)-like surface dimer configurations. This configuration reduces the ordering degree of the growing bulk layer [18].

For the well-defined QWs in figure 1, the thickness and the conduction band offset ΔE_C with respect to InGaP are found to be about 20 nm and −2 meV, respectively. The conduction band offset between InGaP and pseudomorphic InP is about 280 meV [19]. The very small offset of −2 meV would relate to an increase of the In mole fraction in the interlayer by about 4×10^{-3}. But, we have clear evidence for polarization charges around the interlayer (figure 1), i.e. higher ordering degree of the interlayer. Therefore, the band offset of −2 meV is mainly due to the band-gap reduction caused by the higher degree of order. This finding is in agreement with the x-ray diffraction results (not shown here), which do not exhibit any strain caused by composition changes of the interlayer. Further support comes from the PL measurements (figure 2). The detected band offset of the interlayer is too small to give an additional peak in the low-temperature PL spectrum besides the typical band-to-band transitions of ordered and disordered InGaP at 1.937 eV and 1.973 eV, respectively (see curve ‘a’ in figure 2).

Under the chosen conditions for growth and interruptions, interlayers are formed. The influence of a possible In enrichment caused by a segregation effect or by an accumulation from parasitical deposits in the reactor chamber during the growth interruption on the band offset and strain is obviously very small. The band offset stems from a thin lattice-matched InGaP layer with a higher ordering degree.

3.2. InGaP growth interruption under AsH$_3$ stabilization

In order to study the As–P exchange, the InGaP surface was stabilized under AsH$_3$ flux during the growth interruptions. The PL spectrum of such an InGaP layer is shown as curve ‘b’ in figure 2. In addition to the typical band-to-band transitions of ordered and disordered InGaP, peaks around 1.76 eV appear, which are not present in samples with PH$_3$-stabilized interruptions (curve ‘a’ in figure 2), or without growth interruptions. The additional peaks can be assigned to an unintentional interlayer formed as a result of the growth interruption under AsH$_3$.

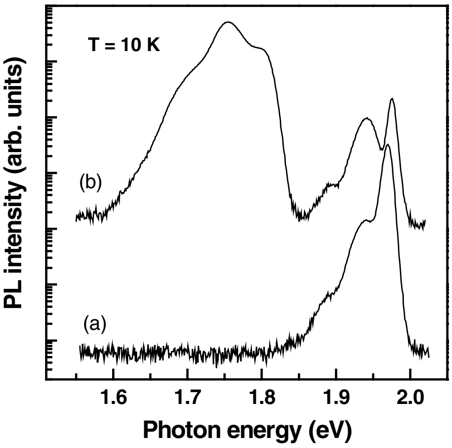

Figure 2. PL spectra measured at 10 K for samples grown with (a) PH$_3$-stabilized and (b) AsH$_3$-stabilized interruptions.

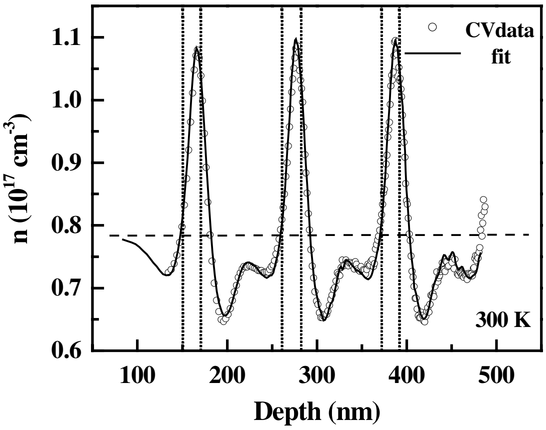

Figure 3. C–V depth profile of the electron concentration n measured at 100 kHz and 300 K for an InGaP layer deposited at 580 °C with several growth interruptions of 60 s under AsH$_3$ flux (circles). Solid line—simulated fit, horizontal dashed line—doping level in InGaP and vertical dotted lines—interface positions of the interlayers according to the simulation.

Figure 3 shows the depth profile of the electron concentration n for the same InGaP layer, which was deposited applying several growth interruptions. The horizontal dashed line marks the Si doping level in the InGaP layer. Remarkable peaks accompanied by strong depletion in both adjacent InGaP regions are present as a result of the growth interruptions. Interlayers are apparently formed under these conditions. Further information on the interlayer is obtained by comparing measured and simulated electron distributions. With the same set of parameters for all interruptions, the fit to the measured electron distribution n is perfect (see line in figure 3). The effective band offset for the interface between the interlayer and InGaP is found to be about −28 meV with an effective interlayer width of about 20 nm.

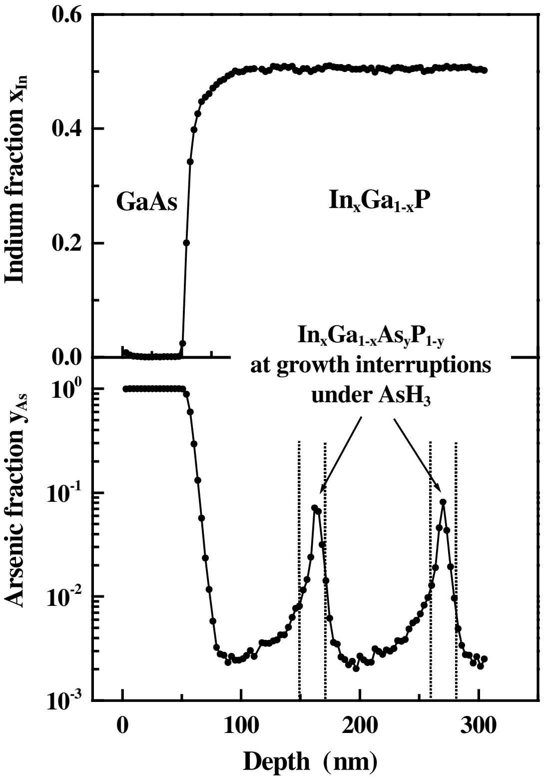

Figure 4. SIMS depth profiles of the In and As concentrations for the InGaP sample capped by GaAs shown in figure 3. Vertical dotted lines—marker for the interfaces of the interlayers from figure 3.

Because it is not clear whether excessive In or As is incorporated during or after the growth interruptions, SIMS depth profiles of the same layer are presented in figure 4. It is evident that the As-related signal is dramatically enhanced at the positions of the growth interruptions, in contrast to the In-related response. As a result of the growth interruption under AsH_3, an As-enriched, compressively strained quaternary (In, Ga) (As, P) interlayer with a smaller band-gap is formed. The positions of the As-related peaks in figure 4 agree with the positions of the maxima of the electron concentration in figure 3. It follows from figure 4 that QWs are formed as a result of growth interruptions. The composition y_{As} gradually changes over a distance of about 20 nm with $y_{As} > 0.01$, in agreement with the n versus depth profiles in figure 3. The SIMS profiles are asymmetrical and show a graded decrease in the As concentration at the upper interface. The region of the highest As concentration y_{As} of about 0.08 can be estimated from the SIMS depth profile in figure 4 to be about 7 nm (3.2 nm steps between measurement points) in accordance with the TEM image in figure 5 (7.5 ± 1.0 nm). It is obvious that the interlayer width obtained from the TEM image (strain contrast) and from simulation of x-ray rocking curves (not shown here) is only connected with the region of highest As concentration, whereas the thickness measured by the C–V method is characteristic for the entire As-enriched region.

It should be noted that there is no indication of any interfacial charges at the heterointerfaces, i.e. these interfaces are defect-free. In particular, polarization charges typical for interfaces with ordered InGaP are missing, in contrast to the growth interruption under PH_3. Therefore, we can conclude that the ordering degree of the InGaP layer is maintained during the formation of the interlayer at growth interruptions under AsH_3, different from the growth interruption under PH_3.

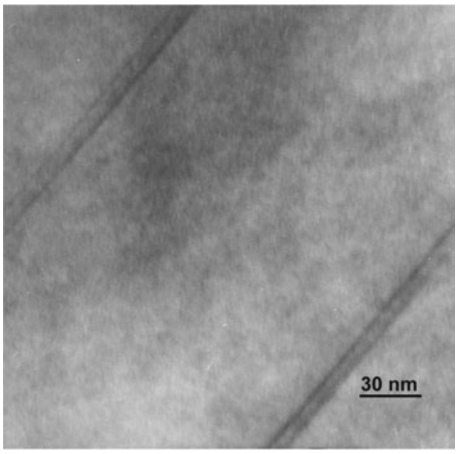

Figure 5. TEM image of the (110) cross-section of the InGaP sample shown in figure 3.

4. Discussion

The surprisingly large thickness of the interlayers found for interruptions under PH_3 and AsH_3 suggests that, besides the As–P exchange, an additional interlayer growth takes place during or/and after the growth interruptions. The conduction band offset of −28 meV detected by the C–V measurement in figure 3 in the case of the arsine-stabilized growth interruption is too small for InGaAs or InAsP interlayers, which could possibly grow during the interruption due to excessive indium on the InGaP surface and/or from hot reactor parts.

From our investigations, it is evident that at a growth temperature of 580 °C and low hydride flows, In carry-over plays a minor role. The growth temperature is so low and the interruption so long that As can be accumulated on the surface during the growth interruptions; it cannot be effectively reduced by desorption [20]. In the case of PH_3 stabilization, the PH_3 supports the formation of the P rich (2×1) surface reconstruction leading to higher ordering during InGaP growth as detected here by the C–V method. It should be mentioned that such changes in ordering can also happen after interruptions of quaternary (In, Ga) (As, P) growth.

During AsH_3-stabilized interruption, arsenic with its greater covalent atomic radius (1.18 Å) replaces the P atoms (1.10 Å) at the InGaP surface only over a few monolayers [9]. The rather gradual decrease of the As concentration after the growth interruption over more than 15 nm seen in figure 4 indicates that the accumulated As at the interface is mainly reduced by an additional As carry-over into the succeeding InGaP layer. This is in contrast to hydride switching at higher growth temperatures, where desorption and As–P exchange dominate and, therefore, thinner interlayers occur (see, i.e. [7, 10]). AsH_3 stabilization at lower growth temperatures leads to an extended, strongly compressively strained (In, Ga) (As, P) interlayer of graded composition. But the effects of P by As exchange, As accumulation and As carry-over can be minimized by reducing the time of arsine stabilization and the AsH_3 flux.

Especially, As accumulation and carry-over are not important when GaAs is deposited onto InGaP. We have studied such interfaces in [21]. For the deposition of GaAs on InGaP, the growth was interrupted for about 5 s by switching-off the TMGa and TMIn flow and then replacing PH_3 directly by AsH_3. TMGa was switched on 0.5 s later. For the InGaP layers grown at 580 °C, PL peak energies of 1.896 eV were measured at room temperature (not shown here). In any case, besides the GaAs-related band-to-band transition of the GaAs substrate, the emission band at about 1.4 eV was missing suggesting sharp heterointerfaces for low V/III-ratios. The C–V depth profile of the electron concentration n for this GaAs-on-InGaP interface did not exhibit any hint to the existence of an interlayer. In contrast, interlayers are observed for longer growth interruptions (see figures 3 and 4) as well as for short interruptions at higher growth temperatures [11].

To avoid group-V carry-over into the following grown layer, the stabilization times with group-V hydrides during the switching sequences should be short. Additionally, low growth temperatures and hydride flows suppress the In carry-over and the As–P exchange.

5. Conclusions

A higher degree of ordering extending over around 20 nm is observed when the MOVPE growth of InGaP is intentionally interrupted under PH_3 flux. The prolonged P-rich stabilization at low growth temperature triggers that ordering, which then decays after growth is resumed. For arsine stabilization during growth interruption, the measurements demonstrate that the inadvertent interlayer is an As-rich (In, Ga) (As, P) layer, the composition y_{As} of which decreases gradually from about 0.08 to 0. The SIMS depth profile shows that, besides As–P exchange, As is carried over into the succeeding InGaP layer after each arsine-stabilized growth interruption. We therefore conclude that at low growth temperatures prolonged purging with arsine should be avoided, before MOVPE GaAs growth on InGaP starts.

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