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Correlation of ordering formation and surface structure in (GaIn)P using modulated MOVPE

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Abstract

Modulated metalorganic vapour phase epitaxial growth (MOVPE) is used to clarify the role of the surface conditions on the ordering behaviour in ternary (GaIn)P layers. The alternating deposition of GaP and InP layers with individual thicknesses of up to one monolayer is successfully used for the growth of (GaIn)P bulk layers lattice matched to (100) GaAs substrates with various off-orientations. The layer quality and the degree of ordering are investigated using high-resolution X-ray diffraction (XRD), transmission electron microscopy (TEM), and photoluminescence spectroscopy (PL), respectively. The application of modulated growth conditions for the deposition of (GaIn)P bulk layers has a strong influence on the degree of ordering achieved in the intermediate growth temperature regime where the highest degree of ordering occurs under continuous MOVPE. Beside a new boundary structure observed in layers grown under modulated flux conditions, the successful growth of highly ordered (GaIn)P layers grown using the modulated MOVPE technique support the model that up to 2 monolayers of the (GaIn)P growth surface are involved in the ordering formation process.

1. Introduction

(GaIn)P is one of the widely used semiconductors for optoelectronic applications such as light-emitting diodes, lasers diodes and solar cells in the visible wavelength range. As reported in the literature, the bandgap energy of a wide range of epitaxial ternary III/V semiconductor alloy layers like (GaIn)P strongly depends on growth conditions and substrate misorientation. These changes in (GaIn)P bandgap energy, which influence the optoelectronic device properties, are due to the spontaneous ordering of these alloys [1–5]. Besides surface diffusivity of the group-III species and growth temperature, the surface structure during growth seems to be the key parameter that determines the degree of ordering [6–9]. In addition, the presence of surface steps influence the degree of ordering [7,10,11]. However, latest theoretical and experimental investigations indicate that surface steps play only an indirect role in the atomic ordering process [12,13].

Ordered (GaIn)P bulk structures are observed for layers grown under modulated group-III flux conditions [13]. Moreover, the degree of ordering of metalorganic vapour phase epitaxial (MOVPE) grown (GaIn)P layers estimated by room-temperature pho-

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toluminescence (RTPL) measurements can be enhanced if modulated flux conditions are used during epitaxial growth. Neither [100] GaP–InP superlattice nor fractional layer superlattice (FLS) structures are observed. Additionally, no surface-step dependence on ordering formation is observed under modulated MOVPE. These experiments support the model that under appropriate growth conditions the formation of ordered structures is mainly determined by the reconstructed surface [13].

However, up to now it is unknown how many subsurface layers are involved in the ordering formation process. As predicted theoretically, up to four subsurface layers (in the following called intermediate layer) corresponding to two monolayers (ML) of (GaIn)P of the reconstructed surface could be involved in the ordering formation process [12,14]. To investigate the intermediate-layer thickness, varying group-III flux conditions were used resulting in the deposition of up to 1 ML of GaP and up to 1 ML of InP per growth cycle corresponding to a deposited (GaIn)P thickness of up to 2 ML per growth cycle.

In this investigation we will present the results of a systematic study of (GaIn)P layers grown with the modulated MOVPE technique in order to determine the influence of the intermediate-layer structure on the ordering process.

2. Experimental procedure

The (GaIn)P epilayers were grown using a commercial horizontal MOVPE system at a reactor pressure of 100 mbar using trimethylgallium (TMGa), trimethylindium (TMIn), and phosphine (PH_3) in a hydrogen carrier gas. The total gas flow through the horizontal reactor was adjusted to 6.8 slm. The V/III ratio was 60, the growth rate was adjusted between 0.34 and 2.33 μm/h, and the growth temperature was chosen between 600 and 650°C. Growth investigations for the present study were performed on semi-insulating GaAs(100) substrates either exactly oriented ((100) $\pm$ 0.25°), or off-oriented by 4° and 5° towards $[0\bar{1}1]$ ({111}B surface steps), respectively. First, a 100 nm GaAs buffer layer was grown using TMGa and AsH_3 to improve the quality of the (GaIn)P epilayer. The thickness of the (GaIn)P epilayers ranged between 0.5 and 2 μm. The thickness of the (GaIn)P layers was measured using a scanning electron microscope.

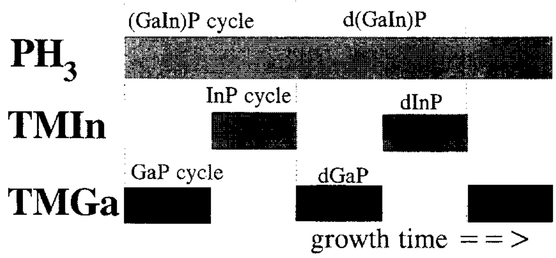

Fig. 1. Gas flow sequence under modulated flux conditions. TMGa and TMIn are introduced alternately into the reactor, to produce up to 1 monolayer (ML) of GaP and up to 1 ML of InP per growth cycle, respectively. The resulting individual GaP (InP) layer thickness d_{GaP} (d_{InP}) per growth cycle and the resulting deposited (GaIn)P layer thickness $d_{(GaIn)P}$ per growth sequence are shown in the picture. Note, that the growth times t_{GaP} and t_{InP} are equal.

The switching sequence of the group-III fluxes during modulated MOVPE is schematically depicted in Fig. 1. In this study the deposited GaP and InP individual layers adjusted between 0.26 and 1 ML per cycle. In the following the individual GaP (InP) layer thickness per growth cycle is labelled d_{GaP} (d_{InP}) or $d_{GaP/InP}$ ($d_{GaP} = d_{InP}$) and the resulting (GaIn)P layer thickness per growth cycle is labelled $d_{(GaIn)P}$. The adjusted growth time per cycle (labelled t_{GaP} or t_{InP} with $t_{GaP} = t_{InP}$) ranged between 0.5 and 2 s and the corresponding (GaIn)P growth time per cycle is labelled $t_{(GaIn)P}$.

For cross-sectional transmission electron microscopy (TEM) the samples were prepared by mechanical thinning and polishing of specimens glued face to face to a thickness of approximately 10 μm, followed by Ar-ion milling at liquid nitrogen temperature. Electron diffraction (ED) as well as dark-field (DF) image studies were performed using a Philips CM 20 microscope. The solid composition of the (GaIn)P epilayers was determined by high-resolution X-ray diffraction (XRD) using a three-crystal diffractometer with Cu Kα_1 radiation. The room-temperature photoluminescence (RTPL) measurements were carried out using the 514.5 nm line of a Ar^+ laser. The luminescence signal was detected with a 1m grating monochromator and a GaAs photomultiplier using the standard lock-in technique.

3. Results and discussion

In this section, first the XRD results will be introduced in which composition, strain, and crystalline perfection of the grown samples are determined. Second, TEM studies are performed to investigate the possible structural changes of the deposited (GaIn)P epilayers such as phase separation, ordering formation, and anti-phase boundary formation. Third, RTPL results will be presented to clarify the role of the modulated growth conditions on the ordering formation process. Finally, the obtained results will be discussed with regard to the intermediate-layer thickness determining the ordering formation process.

The morphology of the investigated samples are mirror like and featureless if (111)B off-oriented substrates are used. For layers grown on exactly oriented (100) substrates, slightly rough surfaces are observed under modulated MOVPE flux conditions. (GaIn)P bulk layers grown using the modulated as well as continuous MOVPE technique show narrow XRD linewidth between 23" and 30" (FWHM) if 4° and 5° (111)B substrates are used. A broadening of the XRD linewidth for layers grown on exactly oriented (100) substrates is observed. The samples investigated here are lattice matched within $\leq \pm 0.1\%$.

The XRD pattern of two (GaIn)P epilayers, grown continuously (top) and under modulated conditions (bottom) on (111)B off-oriented substrates, establishing the high-crystalline perfection of the deposited layers, are shown in Fig. 2 on a logarithmic intensity scale around the (400) reflection of GaAs. If short GaP (InP) growth times per cycle and high group-III flux velocities are used the XRD linewidths are broadened. Probably, increased fluctuations in group-III flux for high fluxes and short switching times result in fluctuations of the solid composition. Therefore, fluctuations of the solid composition are assumed to cause the broadening of the XRD spectra. Additionally, if high group-III flux velocities are used the broadening effect is amplified. However, the observed solid composition fluctuations have only a minor influence on the RTPL linewidth of the layers.

Electron diffraction (ED) patterns and high-resolution transmission electron microscopy (HRTEM) images of the investigated layers prove that ordered (GaIn)P bulk layers are realized under modulated MOVPE [13]. Fig. 3 shows the dark-field (DF) images of two layers grown on 4° and 5° (111)B substrates using modulated flux conditions resulting in (a) $d_{GaP/InP} = 0.26$ ML and (b) $d_{GaP/InP} = 1$ ML. Neither formation of [100] GaP–InP superlattices or FLS are detected nor indication of phase separation effects are found [15] but ordered (GaIn)P bulk structures are observed. As it is clearly seen, typical anti-phase boundary (APB) structures (indicated as A) are observed for both samples which are similar to those observed in continuously grown layers. The APBs correspond to domain boundaries where the ordered planes are shifted about one lattice constant along $[1\bar{1}1]$ or $[11\bar{1}]$.

In addition, the sample with $d_{GaP/InP} = 1$ ML show an additional contrast indicated as B (Fig. 3b). This B structure resulting from a novel anti-phase boundary between ordered domains is never observed in layers grown under continuous flux condi-

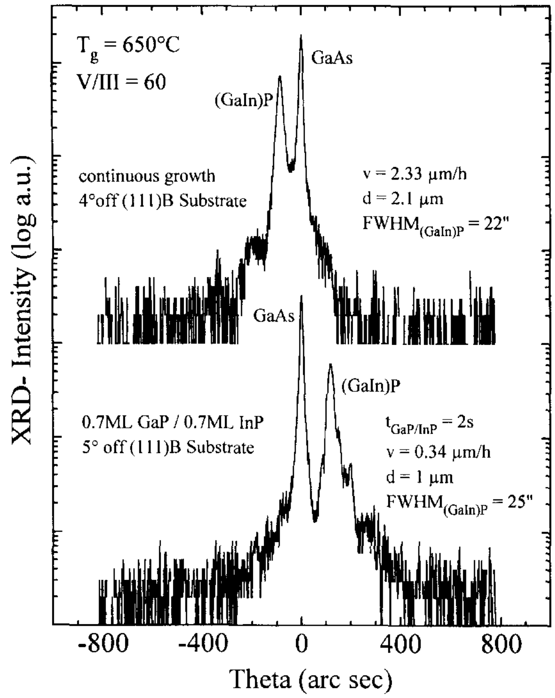

Fig. 2. Typical XRD spectra for layers grown under continuous (top) as well as modulated (bottom) group-III flux conditions.

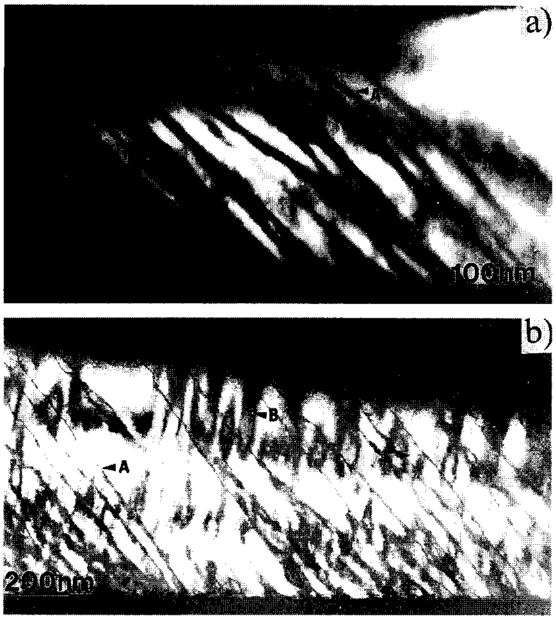

Fig. 3. TEM dark field image of layers grown at t_g = 650°C under modulated flux conditions resulting in the growth of (a) 0.26 ML of GaP and 0.26 ML of InP and of (b) 1 ML of GaP and 1 ML of InP, respectively. The used substrates off-oriented (a) 4° towards $[11\bar{1}]$ {(111)B steps} and (b) 5° towards $[1\bar{1}1]$ {(111)B steps}, respectively. Two types of anti-phase boundary structures are observed indicated by A and B. Neither [100] superlattice nor FLS formation is observed.

tions. A detailed structural analysis of this novel boundary will be published elsewhere [16].

A direct correlation between the degree of ordering and the bandgap energy is predicted for ternary III/V materials, i.e. the higher the degree of ordering the lower the bandgap energy [17]. Therefore, RTPL and absorption measurements are performed as an indirect measure of the degree of ordering. The RTPL spectra are corrected for composition and strain effects [18]. The luminescence efficiency is similar for all investigated layers. The RTPL spectra of five (GaIn)P bulk layers, grown continuously (top) and under different modulation conditions (middle and bottom), on 4° (111)B off-oriented substrates are shown in Fig. 4 on a linear scale. The RTPL energies indicate that all layers are highly ordered. An increase in the degree of ordering is observed with increasing growth rate (middle) in accordance to the dependence under continuous MOVPE at 650°C [6]. The highest degree of ordering is observed for the sample with deposition of precisely 1 ML of GaP and 1 ML of InP per cycle (bottom). The observed PL linewidth broadening of this sample is correlated with a broadening of the distribution of ordered domains with varying degree of ordering [19]. Using absorption experiments the observed red shift of the absorption edge with increasing $d_{GaP/dInP}$ support the RTPL results.

The dependence of the room-temperature bandgap on the GaP (InP) deposition thickness $d_{GaP/InP}$ is summarized in Fig. 5 for layers grown at 650°C. The vertical error bars result from composition fluctuations estimated from the XRD linewidth. For comparison the bandgap energies for samples grown with various growth rates and fixed $d_{GaP/InP} = 0.7$ ML are shown (hollow circles).

With increasing GaP (InP) deposition thicknesses, a strong decrease in RTPL energy independent of the used substrate is observed. Therefore, the preference

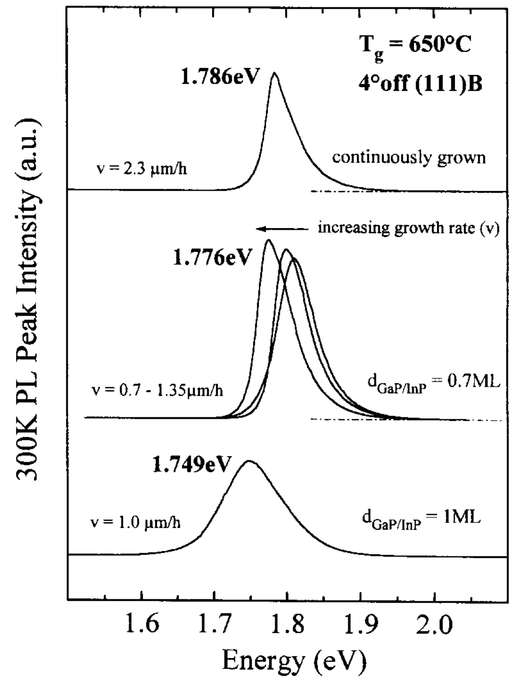

Fig. 4. The RTPL spectra of five (GaIn)P bulk layers, grown continuously (top) and under different modulation conditions (middle and bottom), on 4° (111)B substrates are shown on a linear scale. Note the comparable PL intensities of the layers indicating comparable luminescence efficiencies. The influence on RTPL peak energy resulting from changes in the growth rate are shown in the spectra.

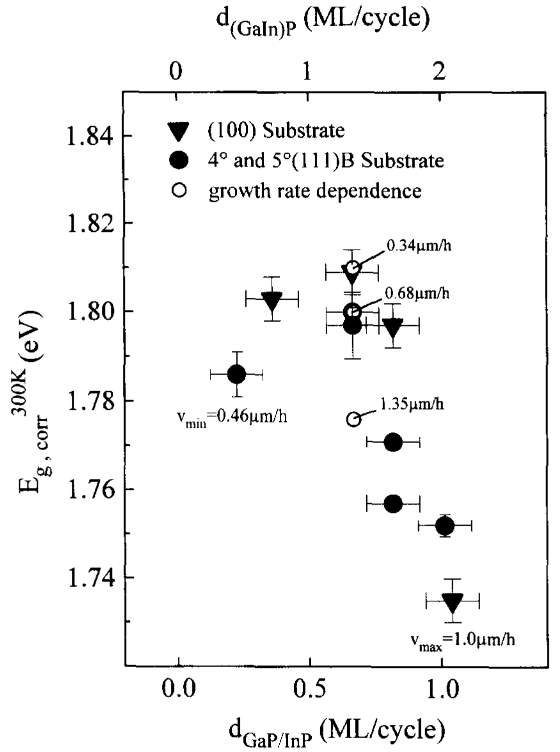

Fig. 5. RTPL energies of layers grown under modulated group-III flux conditions as a function of the real deposited GaP (InP) individual layer thickness. For increasing d_{GaP} (d_{InP}) a decrease in RTPL peak energy, i.e. increase in the degree of ordering, is observed.

of (111)B steps supporting atomic ordering disappears for layers grown under modulated group-III flux conditions [13]. These observations indicate that the surface reconstruction plays a more important role in the ordering process. The highest degree of ordering obtained for the deposition of 1 ML of GaP and 1 ML of InP per cycle would imply that the minimum intermediate layer lies near 2 ML of (GaIn)P. These results are in good agreement with theoretical predictions where strain effects down to the fourth subsurface layer determine the ordering formation process [12,14].

If this model is correct, an increase in bandgap energy is predicted if $d_{GaP/InP}$ is increased above 1 ML. Additional experiments are underway to clarify this point.

4. Summary and conclusion

Modulated MOVPE is used to investigate the role of the intermediate layer on ordering formation. Highly ordered (GaIn)P bulk layers are successfully grown using MOVPE with modulated as well as continuous group-III flux conditions in the temperature range between 600 and 650°C. For all investigated layers no FLS structures as well as no phase separation effects are observed in the transmission ED patterns and DF images, respectively. An additional boundary structure (B boundary) is observed for layers grown under modulated flux conditions with GaP (InP) deposition thickness of more than 0.7 ML.

(GaIn)P bulk layers grown under modulated flux conditions show an additional reduction in RTPL energy as compared to continuously grown layers. Therefore, layers grown under modulated flux conditions show a higher degree of ordering by increasing the GaP (InP) individual layer thickness up to 1 ML per growth cycle (corresponding to a (GaIn)P layer thickness of 2 ML per growth cycle). No dependence on the substrate off-orientation is detected. These observations indicate that the surface reconstruction plays a more important role for the ordering process in the studied intermediate growth temperature range.

These results are in good agreement with theoretical predictions [12,14] that up to 2 ML of (GaIn)P (four uppermost layers) are involved in the ordering formation process.

Acknowledgements

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