Spinodal-like decomposition of InGaP epitaxial layers grown on GaP substrates

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Abstract

The spinodal-like decomposition of In₀.₅₆Ga₀.₄₄P epitaxial layer prepared by low-pressure metalorganic vapour phase epitaxy was studied by means of photoluminescence and transmission electron microscopy. Epitaxial layers were grown on GaP substrates at T_g = 740 °C and reactor pressure of 20 mbar. We show that presence of spinodal-like decomposition occur at samples with InP mole fraction higher as x = 0.2 and V/III ratio of 75. The low-temperature photoluminescence spectra shows that in partially decomposed samples a characteristic broad band occurred close to 1.985 eV. An increase in the V/III ratio up to a value of 350 suppressed the decomposition, and PL signal with only one narrow transition was obtained.

Keywords: Spinodal; Decomposition; MOVPE; Epitaxy; InGaP alloy

1. Introduction

The growth of III–V compound semiconductor alloy systems is considered to be important because of possible applications in many electronic and optoelectronic devices. InₓGa₁₋ₓP alloys offer the potential of direct recombination luminescence materials throughout the visible spectrum from the red almost to the green. This makes this material so attractive that the understanding of the phase equilibria and possible phase separation are of particular interest. InGaP, like many other III–V compounds, is thermodynamically unstable. It exhibits a miscibility gap and a tendency to clustering and phase separation. Phase separation on the surface of an epitaxial layer during growth is quite different from conventional spinodal decomposition observed in alloys. The free energy of an alloy is lowered by compositional fluctuations in the bulk of its crystal, which is separated into phases at a certain critical temperature. By metalorganic chemical vapour phase epitaxy (MOVPE) it is possible to prepare nearly metastable alloys with composition within the miscibility gap. Spinodal decomposition does not proceed into the bulk of a material because of low diffusion coefficients in III–V semiconductors and relatively high growth rates, but its influence is often observable on the
surface of a layer grown. The separation on the surface of an epitaxial layer requires that the surface free energy be lowered by elemental segregation. The term “spinodal-like” decomposition is usually used to distinguish the surface localized spinodal decomposition during epitaxial growth from alloy decomposition occurring during equilibrium crystal growth. Phase separation is not understood as well as ordering, but it similarly needs to be controlled since compositional variations can influence PL emission spectra or other parameters [1].

In this paper we report on a study of the spinodal-like decomposition of In$_x$Ga$_{1-x}$P grown on (100) GaP substrates at 740 °C by MOVPE. We concentrated our efforts on an alloy with the InP mole fraction close to $x_{\text{In}} = 0.27$, at which the indirect-to-direct band gap structure crossover occurs and at which the direct band gap energy is sufficiently high for green photoluminescence. Because of all these InGaP layers were predicted to be applied in graded buffer growth on GaP substrates it was necessary to find compromise in growth conditions and to find the growth conditions (growth temperature, reactor pressure, V/III ratio) acceptable for both systems.

2. Spinodal decomposition in InGaP

Phase separation originates from spinodal decomposition, which is kinetically allowed at the surface. Wei et al. [2] calculated critical temperatures for miscibility gaps for many ternary compounds including the In$_x$Ga$_{1-x}$P alloy. The critical temperature calculated for In$_x$Ga$_{1-x}$P is well below typical growth temperatures at which compositional modulation is observed. In general, compositional modulation can occur only when surface diffusion coefficients are sufficiently high to allow for the initialization of surface separation during growth. Compositional modulation depends on growth temperature [3], growth rate [4], and surface roughness [5]. Ginoudi et al. [6] observed in a TEM analysis of InGaP samples grown by MOMBE and MOVPE two types of compositional modulation. One type oriented nearly vertically to the interface (i.e. parallel to the growth direction) is attributed to spinodal decomposition. The other type of modulation parallel to the growth interface (lateral modulation) has been attributed to micro-scale compositional variations due to instabilities of growth conditions [7]. Follsteadt et al. [8] studied a microstructure of InGaP grown on GaAs substrates in a temperature range of 660–775 °C. The TEM and photoluminescence examinations shows that phase separation was observable, independently of ordering, for the entire range of growth parameters. TEM contrast shows modulations with a variable spacing ranging from a few nanometers to 100 nm. Ordering can be eliminated by growth at 750 °C or above. Schuler et al. [9] studied the spinodal decomposition of InGaP layers grown by GSMBE. They found that at a growth temperature of 520 °C spinodal domain were sized between 0.17 and 0.5. It meant that the alloy composition of In$_x$Ga$_{0.8}$P was very close to the spinodal curve for the low In content, which implied that in this case spinodal decomposition played no important role. However, in the In$_x$Ga$_{0.7}$P alloy the spinodal decomposition of the alloy should result in the formation of In$_{0.5}$Ga$_{0.5}$P and In$_{0.17}$Ga$_{0.83}$P alloys. The tensile strained layers were more influenced by spinodal decomposition.

3. Experimental

Undoped InGaP epitaxial layers were grown by a low-pressure metalorganic chemical vapour phase epitaxy (MOVPE) technique. Trimethylgallium (TMGa), trimethylindium (TMIn) were used as group III precursors and phosphine (PH$_3$) as the group V source. A series of samples with increasing molar ratio of indium phosphide $x_{\text{In}}$ was prepared in order to study the properties of In$_x$Ga$_{1-x}$P layers grown on (0 0 1) oriented GaP substrates as a function of $x_{\text{In}}$. Compressively strained layers with a thickness of 1.2 µm were deposited directly on GaP substrate. Growth parameters were initially optimized to avoid the tendency to 3D growth (creation of hexagonal hillocks) in GaP and In$_x$Ga$_{1-x}$P with low $x_{\text{In}}$. Based on a growth optimization process described in [10], we chose for the present experiment the growth temperature ($T_g$) of 740 °C, growth rate of 0.8 µm/h, and the reactor pressure of 20 hPa. For the growth of GaP and a low $x_{\text{In}}$ content In$_x$Ga$_{1-x}$P the optimum V/III ratio was 74. For the last sample investigated, the V/III ratio was changed to 348 for the reasons explained below. Table 1 summarizes all layers under investigation. The growth temperature of 740 °C is convenient on GaP.
surface but it also makes the evaluation of phase separation in InGaP much simpler because ordering should be suppressed at this temperature.

The solid composition of the InGaP layers was determined from X-ray diffraction measurements using Cu Kα radiation. In order to obtain some information about the band gap energy of the layers, their low-temperature photoluminescence spectra were measured at $T = 5$ K under excitation at 488 nm from an Ar ion laser. The laser beam was focused at normal incidence to a spot, at which its intensity was 1 W/cm². The luminescent signal was filtered using a quarter-meter monochromator, and it was detected by a silicon photodiode using a standard lock-in technique. Cross-sectional layer structure was examined by transmission electron microscopy. TEM investigations were performed using (1 1 0) cross-section slides prepared by gluing of two InGaP surfaces together. The samples were thinned by polishing and Ar⁺ ion milling.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>V/III ratio</th>
<th>InP mole fraction, $x$</th>
<th>PL mean peak (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>74</td>
<td>0.157</td>
<td>2.314</td>
</tr>
<tr>
<td>B</td>
<td>74</td>
<td>0.258</td>
<td>2.270</td>
</tr>
<tr>
<td>C</td>
<td>74</td>
<td>0.276</td>
<td>1.945</td>
</tr>
<tr>
<td>D</td>
<td>348</td>
<td>0.279</td>
<td>2.222</td>
</tr>
</tbody>
</table>

Fig. 1. Photoluminescence spectra of InGaP samples under study. All samples were grown on GaP substrate at 740 °C and a V/III ratio of 74.

### 4. Results

At first we investigated low-temperature photoluminescence spectra of In$_x$Ga$_{1-x}$P samples with the InP mole fraction $0 < x_{In} < 0.28$. Fig. 1 compares photoluminescence signals from three InGaP epitaxial layers grown on GaP substrate. The spectra were normalized to the same maximum intensity. Sample A ($x_{In} = 0.157$) shows photoluminescence signal typical for InGaP with an indirect band gap structure. This GaP like spectrum is dominated by the main transition at 2.314 eV, which is ascribed to the recombination of an exciton bound to a neutral donor. This transition is broader than a similar transition, which we usually observe in our GaP epitaxial layers (full width at half maximum is about 15 meV compared with 9 meV in GaP). At lower energies two phonon assisted replicas are shifted each by 48 meV. Another sample that shows a GaP-like photoluminescence response was grown with $x_{In} = 0.258$. Photoluminescence of this sample is similar to that of the previous one, but the dominant transition lies at 2.270 eV, and another very broad weak peak with a maximum close to 1.945 eV occurred. The presence of a peak of such type is
usually connected with the existence of some defect level [11], with ordering, or with the formation of a thin epitaxial layer of another composition [12].

Further increase in the InP mole fraction to $x_{\text{In}} = 0.276$ in sample C led not only to a drastic increase in photoluminescence intensity but also to a change in the shape of PL spectrum. It consists of one peak that is very similar to the photoluminescence of InGaP layers with a direct band gap structure grown on GaAs substrates. The significant increase of PL intensity and the change of spectrum type from GaP-like to InGaP-like (or InP-like) indicate that this sample exhibits a direct band gap structure. On the other hand, the position of this peak at 1.85 eV is too far from the expected energy value of 2.20 eV [13]. Also, its width of FWHM = 154 meV indicates that it includes more transitions. Fig. 2 shows a deconvolution of this photoluminescence signal into five various Gaussian peaks. From this figure it follows that the dominant transition is at 1.945 eV. It indicates that a material with the same or very similar composition exists in both samples B and C. As the presence of ordering may be excluded at growth temperature as high as 740°C, this band gap value indicates a material with a dominant InP mole fraction of $x \sim 0.5$, i.e. a material close to the GaAs lattice matching.

With the aim to bring more light into this problem, we used transmission electron microscopy to study the uniformity of our samples in cross-sectional views. The TEM observations revealed that sample A with $x = 0.15$ was uniform. A network of misfit dislocations was only observable at the interface with the GaAs substrate (see Fig. 3a). All the samples examined with TEM shows contrast indicating that the composition varied within the layers. Fig. 3b shows a cross-sectional view of sample B with an InP mole fraction of $x = 0.258$. In this layer we observed intensive contrast modulation, which can be described as sharp and black areas oriented almost vertical to the interface. They are mostly concentrated in bottom part of the layer and they start from the interface. This contrast modulation is attributed to compositional fluctuation connected with spinodal-like decomposition. Fig. 3c shows a TEM cross-sectional view of sample C ($x = 0.276$). The effect of compositional separation is very extended in this case. The black areas are almost parallel with the growth direction, and they are broader at the interface, but in many cases they pass through the whole epitaxial layer. In addition, one can also observe a very fine multilayer structure parallel with the substrate–epitaxial layer interface in small and exactly limited areas. This type of structure modulation indicates micro-scale instabilities of growth conditions during the growth of the epitaxial layer [6].

The photoluminescence and TEM observations indicated that for the epitaxial growth of InGaP up to
Fig. 3. TEM cross-sectional images of spinodal-like contrast in the InGaP layers. (a) sample A with $x = 0.157$, (b) sample B with low level of spinodal-like decomposition, and (c) sample C with spinodal-like decomposition through whole layer width from interface up to surface.
For higher InP mole fraction values, it is necessary to increase the V/III ratio also. Fig. 4 shows the photoluminescence signal obtained from an InGaP epitaxial layer grown at a V/III ratio of 350. Correspondingly to this V/III ratio increase, the PL FWHM decreased significantly to 30 meV. The photoluminescence signal consists from one transition at 2.222 eV typical for a direct band gap structure. The position of this dominant transition corresponds with the dependence of band gap energy on InGaP composition. We suppose that the relatively higher FWHM value may be ascribed to strain connected with high lattice mismatch ($x = 0.279$). The presence of high amount of phosphorus atoms at the surface may lead to the formation of a (2 × 1) surface reconstruction with lines of phosphorus dimers, and consequently to ordering [13]. With the aim to prove or to exclude this assumption, we measured a dependence of the photoluminescence peak position on laser excitation intensity. In ordered InGaP a blue shift of dominant photoluminescence transition is usually observed. This emission shift is caused by the filling effect of band-tail states. By means of a neutral density filter we varied the excitation power for PL measurements but no blue shift typical for the presence of ordered domains was observed [14]. The growth temperature of 740 °C is obviously sufficiently high to prevent the ordering effect.

5. Conclusions

The spinodal-like decomposition of InGaP epitaxial layers grown at 740 °C by MOVPE was studied by means of photoluminescence and TEM. Both methods revealed that for the epitaxial growth of InGaP up to $x = 0.2$, the V/III ratio value close to 80 can deliver a sufficient amount of phosphorus to grow uniform layers. Further increase in the InP mole fraction $x$ (at the same value of V/III ratio) led to the growth instability connected with spinodal-like decomposition and compositional fluctuations. Both effects are reflected in TEM views as contrast modulations parallel and vertical to the growth direction. The spinodal domains are parallel with the growth direction and they start from the interface between epitaxial layer and substrate usually. We suppose that high lattice mismatch can cause a surface roughness sufficiently high to start a partial elastic relaxation and to allow spinodal-like decomposition at the grown surface. This effect may be suppressed by additional presence of phosphorus atoms at the grown surface. The low-temperature photoluminescence spectra shows that in partially decomposed samples a characteristic broad band occurred close to 1.985 eV. An increase in the V/III ratio up to a value of 350 suppressed the decomposition, and PL signal with only one narrow transition was obtained.

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References