Growth and characterization of Ga$_{0.65}$In$_{0.35}$P orange light-emitting diodes by metalorganic vapor–phase epitaxy

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$p$–$n$ Ga$_{0.65}$In$_{0.35}$P homostructure light-emitting diodes grown on GaAs$_{0.7}$P$_{0.3}$ substrates have been fabricated by low-pressure metalorganic vapor-phase epitaxy. The growth and characterization of undoped, Si-, and Zn-doped layers are described in detail. The optimum growth condition to grow the high-quality Ga$_{0.65}$In$_{0.35}$P epitaxial layers is at the growth temperatures of 700–740 °C and V/III ratios of 100–200. The strongest photoluminescence peak intensity occurs at $2 \times 10^{18}$ and $7 \times 10^{17}$ cm$^{-3}$ for electron and hole concentrations, respectively. Diodes fabricated from the $p$–$n$ homostructure are characterized by current-voltage measurement, electroluminescence, and external quantum efficiency. A forward-bias turn-on voltage of 1.68 V with an ideality factor of 2.5 and a breakdown voltage of 9 V are obtained from the current-voltage measurements. The emission peak wavelength and full width at half-maximum of electroluminescence are around 610 nm and 79 meV at 20 mA. The external quantum efficiency of the uncoated diode is about 0.015%.

I. INTRODUCTION

Visible semiconductor lasers in the 600 nm wavelength region are very attractive as light sources in the fields of optical information-processing systems such as optical disk memories and audio/video disk equipments. Shortening of the lasing wavelength is expected to expand the application area to plastic optical fibers for the local information networks. The shortest wavelength achieved at present for the well-developed AlGaInP/GaInP system lattice matched to GaAs substrate is 620–670 nm. Therefore, the growing demands for the shorter-wavelength light sources have stimulated the interest in a new category of III–V semiconductor materials. Gallium indium phosphide Ga$_{1-x}$In$_x$P ternary compound semiconductor, which has been extensively studied, is a potential candidate for visible-light-emitting applications because of its direct band gap as high as 2.25 eV ($x=0.74$) at 300 K and containing no aluminum. It can offer, in principle, an opportunity to fabricate efficient light emitters in the red-to-green region of the visible spectrum. It can be grown on commercial GaAs$_{0.7}$P$_{0.3}$ substrates with exact lattice match at a composition of 65% GaP and a band gap of about 2.115 eV (586 nm in wavelength). Some degree of success in growth of Ga$_{1-x}$In$_x$P has been achieved by several epitaxy techniques including liquid-phase epitaxy (LPE) and hydride vapor-phase epitaxy (VPE). Recently, much more attention has been paid to metalorganic vapor-phase epitaxy (MOVPE) due to the excellent control of composition and layer thickness, and suitability for economical mass production. Kondo et al. succeeded in the preparation of GaInP light-emitting diodes (LEDs) operated in the 600 nm region on Si substrates using GaAsP/GaAs buffer layers. Masselink and Zachau fabricated LEDs with peak emission centered at less than 590 nm from $p$–$i$–$n$ junctions in Ga$_{0.65}$In$_{0.35}$P grown by gas-source molecular-beam epitaxy. However, only a few reports have been published regarding MOVPE growth of the Ga$_{0.65}$In$_{0.35}$P/GaAs$_{0.7}$P$_{0.3}$ alloy system for wide-band-gap applications. Yuan et al. reported the growth and characterization of Ga$_{1-x}$In$_x$P ($x=0.51$, 0.65, and 0.69) to obtain an optimum growth temperature 625 °C and an optimum V/III ratio (the molar ration of the column-V source to the column-III sources in the reactant gas) range of 40–50; but, there are no reports on the devices consisting of the Ga$_{0.65}$In$_{0.35}$P alloy prepared by MOVPE.

In this article we present the growth and characterization of undoped, Si-, and Zn-doped Ga$_{0.65}$In$_{0.35}$P layers on GaAs$_{0.7}$P$_{0.3}$ substrates by low-pressure metalorganic vapor-phase epitaxy (LP MOVPE). The effects of growth temperature and V/III ratio on the band-gap energy anomaly, which can be ascribed to the order structure of the group-III sublattice just as observed in Ga$_{0.65}$In$_{0.35}$P (Refs. 19–21) and Ga$_{0.65}$In$_{0.35}$P alloys, are presented. The fabrication and performance of Ga$_{0.65}$In$_{0.35}$P $p$–$n$ homostructure LEDs emitting in the orange (620 nm) region at 300 K are reported for the first time.

II. GROWTH AND CHARACTERIZATION OF UNDOPED, SI-, AND ZN-DOPED Ga$_{0.65}$In$_{0.35}$P LAYERS

Ga$_{0.65}$In$_{0.35}$P epitaxial layers were grown by LP MOVPE in which a graphite susceptor was heated by an infrared (IR) strip heater in a horizontal quartz reactor, as described in an earlier publication. The metal-alkyl sources employed were trimethylgallium (TMGa) with a bubbler temperature of -12.4 °C and a pressure of 500 mbar, and trimethylindium (TMIIn) with a bubbler tem-
perature of 17 °C and a pressure of 200 mbar, for which the vapor pressures have been found to be 90.1 and 8.8 mbar, respectively. 100% phosphine (PH₃) is used as the phosphorous source. Disilane (Si₂H₆) and dimethylzinc (DMZn) were used as n- and p-type dopants, respectively. The substrates were GaAs₀.₇P₀.₃ commercial epitaxial wafers grown by VPE on Si-doped (100) GaAs substrates two off toward (110). A 30-μm-thick graded composition of GaAsP layer is used between GaAs and the GaAs₀.₇P₀.₃ layer to avoid a large lattice mismatch. The surface GaAs₀.₇P₀.₃ layer is 40 μm thick and n doped to 3×10¹⁷ cm⁻³ with Te. Before loading into the reactor, the GaAsP substrate was prepared by etching in a 5:1:1 H₂SO₄:H₂O₂:H₂O for 90 s at room temperature. The precursors were carried by Pd-purified H₂ with a total flow rate of 6.7 s/min. The reagents were injected into the reactor through a high-speed vent/run gas switching manifold. The reactor was kept at 50 mbar with infrared heating and the substrate was rotated at 100 rpm during epitaxial growth. Different growth conditions including growth temperature ranging from 620 to 780 °C and the V/III ratio varying from 80 to 300 were employed. A 1.3-μm-thick Ga₀.₆₅In₀.₃₅P layer was grown directly on the substrate without a buffer epitaxial layer for the typical growth rate of 2.7 μm/h.

Nomarski-phase-contrast microscope, double-crystal x-ray-diffraction, capacitance-voltage (C-V), and photoluminescence (PL) measurements were carried out to characterize the undoped and doped GaInP layers. Details of growth conditions and characterization techniques are given elsewhere.²⁴²⁵

For all the undoped and doped GaInP samples, the surface morphology is very flat and mirrorlike, with a so-called cross-hatch-pattern surface, which is inherited from the original misfit dislocations introduced during the graded layer growth of GaAsP on the GaAs substrate.²⁶²⁷ The interface between epitaxial layer and GaAs₀.₇P₀.₃ substrate is also flat and free from inclusions. Lattice mismatch, determined by (400) reflection planes of a double-crystal x-ray diffractometer using the CuKa₁ line, between the epitaxial layer and GaAsP substrate normal to the wafer surface, is controlled to be within ±0.08%. The solid composition x of GaIn₁₋ₓP epitaxial layers is 0.65, as measured from the lattice-mismatching degree by assuming Vegard's law. The carrier concentration of the GaInP epitaxial layers was evaluated by the C-V method. The Schottky barrier was formed with liquid-mercury metal by a mercury-probe station. Unintentionally doped GaInP layers always exhibit n-type conduction with the background electron concentration of 8×10¹⁵ cm⁻³. Photoluminescence spectra were measured at 20 and 300 K by exciting the wafers at an intensity of about 4 W/cm² with a 488 nm line from an Ar⁺ laser. In general, they both show only one emission peak related to a near-band-gap transition and no other impurity peak is observed. Figure 1 shows the PL peak energy and full width at half-maximum (FWHM) of the GaInP epitaxial layers at 20 and 300 K as a function of the growth temperature Tg while the V/III ratio is kept at 100. Both the peak-energy curves have a higher energy of 2.150 eV at 20 K and 2.075 eV at 300 K for the case of Tg=620 °C and decrease rapidly to a minimum value of 2.057 eV at 20 K and 2.007 eV at 300 K for Tg=680 °C. After passing over this minimum point, with increasing growth temperature, the peak-energy curves rise again. The peak energy of 2.153 eV at 20 K and 2.076 eV at 300 K is reached at Tg=780 °C. Outside this range of temperatures investigated, the PL intensity is too weak to be detected and the surface morphology is seriously deteriorated for the MOVPE-grown samples. On the other hand, the PL FWHM curves exhibit a minimum value of 19 meV at 20 K and 48 meV at 300 K at the growth temperatures between 700 and 740 °C, which is just the case that can obtain the lowest carrier concentration of 8×10¹⁵ cm⁻³. At the growth temperature of 680 °C, they present a broader PL FWHM value of 23 meV at 20 K and 56 meV at 300 K. When the growth temperature is below 700 °C or above 740 °C, the PL FWHM will be further increased. Figure 2 shows the PL peak energy and FWHM of the GaInP at 20 and 300 K as a function of the V/III ratio at the growth temperature of 740 °C. The PL peak energy monotonically decreases with increasing V/III ratio. The difference for 300 K PL peak energies of GaInP, grown with V/III ratio=80 and 300, is about 29 meV. Both FWHM curves exhibit the narrow values of 18 and 56 meV at 20 and 300 K, respectively, in the V/III range from 100 to 200. Outside the V/III range, the FWHM value increases slightly.

When the GaInP epitaxial layers were grown at the growth temperatures below 650 °C for the constant V/III of 100 (as shown in Fig. 1) or at the V/III ratios below 100 for Tg=740 °C, these samples always exhibited a rough surface morphology and a very weak PL intensity due to the insufficient decomposition of PH₃, even though they may have a narrower PL FWHM at the lower growth
temperatures as shown in Fig. 1. The observed increase in the PL FWHM at higher growth temperatures (for the case of Fig. 1) is explained by the ease depletion of In atoms in the GaInP-grown layer. From the above observations in Figs. 1 and 2 we can find that GaInP layers, lattice matched to GaAs0.7P0.3 substrates and grown with different Tg or V/III ratios, have different band-gap energies. This indicates that GaInP with the same alloy composition can have different band-gap energies. The theoretical band gap of GaAs0.65In0.35P can be calculated as 2.101 eV at 300 K by fitting the value of x=0.65 into the following equation:

$$E_g = 1.351 + 1.429x + 0.786x(x - 1).$$

Fujimoto et al.\textsuperscript{7} reported that the LPE-grown GaAs0.7In0.3P layers have a 300 K band gap of 2.105 eV from PL measurements. The lower-band-gap energy of MOVPE-grown samples in this study is mainly caused by the CuPt-type ordered structure in which the column-III constituent atoms are periodically distributed on a corresponding face-centered-cubic sublattice.\textsuperscript{20,29} Generation of an ordered structure can be attributed to either the thermodynamic stabilization or growth kinetics.\textsuperscript{20-23} This ordering structure is also reported for the GaAs0.7In0.3P (Refs. 19-21) and GaAsP (Refs. 22 and 23) alloys lattice matched to GaAs and GaAsP, respectively. Valster et al.\textsuperscript{24} reported that a significant reduction of PL FWHM and the ordering effect can be obtained by growing the GaAs0.7In0.3P layer on the (311)B-oriented substrate at the constant growth temperature and V/III ratio.

All the above observations indicate that the optimum growth condition to grow high-quality GaAs0.65In0.35P epitaxial layers by MOVPE is at Tg=700–740°C and V/III =100–200.

Both the Si and Zn atoms of dopants Si$_2$H$_6$ and DMZn occupy the group-III atom sites in the GaInP lattice to act as the donor and acceptor, respectively. Therefore, the doping efficiency should depend on the effective molar flow-rate ratio [Si$_2$H$_6$]/[III] or [DMZn]/[III] onto the substrate and also on the surface absorption characteristics of GaInP. Figure 3 shows the dependence of room-temperature carrier concentration (n or p) on the molar flow rate of Si$_2$H$_6$ or DMZn to the total group-III sources, [Si$_2$H$_6$]/[III] or [DMZn]/[III], and the Si- or Zn-doped GaAsIn0.35P layers grown at Tg=740°C and V/III=100. When the molar flow rate of the dopants is increased, the carrier concentrations increase as the 0.90th and 0.85th power of [Si$_2$H$_6$] and [DMZn] for the GaAsIn0.35P alloy, respectively. The slopes in the log-log plot of incorporated dopant versus the partial pressure of the dopant gas is consistent with the proposed range between 0.5 and 1 which is reported by Giling and deMoor.\textsuperscript{33,34} It is clear that high doping concentrations in excess of 10$^{18}$ cm$^{-3}$ can easily be obtained for both n- and p-type materials. In the range studied, 1×10$^{-4}$ < [Si$_2$H$_6$]/[III] < 5×10$^{-3}$, the electron concentration increases from 3×10$^{17}$ to 6×10$^{18}$ cm$^{-3}$. With further increasing [Si$_2$H$_6$]/[III], the electron concentration saturates at a value near 7×10$^{18}$ cm$^{-3}$. The saturation of electron concentration occurs as a consequence of the decreasing electrical activity of Si impurities in the solid. This saturation level is in good accordance with the saturation levels of 5×10$^{18}$ cm$^{-3}$ reported for Si-doped GaAs0.7In0.3P grown at 690°C by using Si$_2$H$_6$.\textsuperscript{35} Hotta and co-workers\textsuperscript{36} reported that the complex centers formed by a Si donor and a Si acceptor (Si$^{+4-}$-Si$^{+3}$) and Si donor and vacancy (Si$^{-}$-V$_{III}$) contribute to the saturation level at high Si atomic concentrations. On the other hand, as [DMZn]/[III] varies from 10$^{-1}$ to 2, the hole concentration increases from 2×10$^{17}$ to 3×10$^{18}$ cm$^{-3}$ and does not saturate even at the high [DMZn]/[III] of 2. The segregation coefficient of the dopant Si or Zn, k$_{Si}$ or k$_{Zn}$, can be defined as the ration of n or p to the group-III lattice sites divided by the ratio of the Si$_2$H$_6$ or DMZn concent-

FIG. 2. PL peak energy and FWHM at 20 and 300 K of GaAs0.65In0.35P layers vs V/III ratio. Growth temperature was kept at 740°C.

FIG. 3. The room-temperature carrier concentration (n or p) of Si- or Zn-doped GaAs0.65In0.35P layers vs mole ration of Si$_2$H$_6$ or DMZn to the total sources group-III sources, [Si$_2$H$_6$]/[III] or [DMZn]/[III].
carrier concentration to the group-III source concentration in the gas phase. At a doping level of $1 \times 10^{18} \text{ cm}^{-3}$, $k_S$ and $k_Zn$ of Ga$_{0.65}$In$_{0.35}$P grown at 740°C to be 0.045 and $5.4 \times 10^{-5}$, respectively. These values are in agreement with the reported values of $k_S \sim 0.2$ at 690°C, $k_Zn \sim 2 \times 10^{-4}$ at 680°C, and $k_Zn \sim 2 \times 10^{-5}$ at 730°C (Ref. 38) in Ga$_{0.3}$In$_{0.7}$P alloys.

Similar to the 20 K PL spectra of the undoped Ga$_{0.65}$In$_{0.35}$P layers, typical 20 K PL spectra of the Si-doped layers also show one emission peak but with a wider FWHM and a lower peak energy. This indicates that the donor ionization energy is very small and tends to merge with the conduction-band states. However, the low-temperature PL spectra of the Zn-doped layers are dominated by a broad emission band arising from two partially resolved peaks which is merged by the near band-to-band and donor-to-acceptor transitions. When the temperature is increased, the increased rate of thermal release of electrons from donor sites or holes from acceptor sites leads to a decrease in the number of bound electrons or holes, and decrease in the donor-to-acceptor recombination rate. Therefore, only one emission band due to the recombination of free electrons and free holes is observed in the room-temperature PL spectra for both the Si- and Zn-doped Ga$_{0.65}$In$_{0.35}$P layers, as seen from the emission band due to free-electron-to-free-hole transition in the undoped Ga$_{0.65}$In$_{0.35}$P layers. The PL peak energy of the Si- and Zn-doped GaInP layers is slightly larger than that of 2.018 eV for the undoped layers. It increases slowly with increasing carrier concentration because the effect of ordered structure will be weakened at high doping levels. The FWHM also increases with increasing carrier concentration. The relative intensity of 300 K PL peaks in Si- and Zn-doped Ga$_{0.65}$In$_{0.35}$P layers as a function of carrier concentration is shown in Fig. 4. The relative PL intensity slightly increases with carrier concentration and approaches a maximum value near $2 \times 10^{18}$ and $7 \times 10^{17}$ cm$^{-3}$ for Si- and Zn-doped layers, respectively. With any further increase in both the carrier concentrations, the intensity drops gradually for Zn-doped layers but it falls off rapidly for Si-doped layers. The observed reduction in the PL intensity of radiative recombination at high carrier concentrations may be explained by the appearance of precipitates (e.g., Zn$_2$P$_2$) or nonradiative deep centers. If the significant density of precipitates or deep centers contributes to lowering the radiative efficiency, then the "useful" dopant solubility for luminescence purposes is clearly limited to the maximum intensity value in the carrier-concentration range around $2 \times 10^{18}$ cm$^{-3}$ for Si-doped layers and $7 \times 10^{17}$ cm$^{-3}$ for Zn-doped layers.

III. FABRICATION AND PERFORMANCE OF p-n Ga$_{0.65}$In$_{0.35}$P LEDs

The p-GaInP/n-GaInP homostructure was grown by LP MOVPE on a (100)-oriented n-type GaAs$_{0.7}$P$_{0.3}$ substrate. The first grown layer is a 2.7-μm-thick GaInP layer. It is an n-type Si-doped layer with an electron concentration of $2 \times 10^{18}$ cm$^{-3}$ which has the maximum PL relative intensity in the electron concentration. The second layer, where most radiative recombinations take place, is a 2.7-μm-thick Zn-doped GaInP layer with a hole concentration of $7 \times 10^{17}$ cm$^{-3}$. In addition, a p-type heavily doped (3.5 $\times 10^{18}$ cm$^{-3}$) layer was sequentially grown to be used as the current spreading layer. The growth temperature and V/III ratio used were 740°C and 100, respectively.

After the growth process, the substrate side was thinned to about 200 μm in order to reduce the bulk resistance. After wafer cleaning, Au/Ni/AuGe with a thickness of 200/10/100 nm was evaporated on the substrate side to form the n contact. For the p contact, a 100 nm layer of AuBe was evaporated onto the p-GaInP layer and patterned into 100-μm-diam dots by lithographic procedures. After deposition, the wafer was alloyed at 450°C for 5 min in a nitrogen ambient to obtain good ohmic contacts. Then a 1 μm Au layer was evaporated over the coated contact on the p side of the wafer for bonding. The top Au metal outside the p contact area was again chemically etched away using 10 g KI: 1 g I$_2$: 100 cm$^3$ H$_2$O through a defined pattern by photolithography to allow light emission through the top of the die. The wafer was next sawed into the die dimension of 400×400 μm$^2$. The chip was then attached and bonded to a TO-5 package for measurements.

A typical current-voltage (I–V) characteristic of the homostructure diode at room temperature is shown in Fig. 5. It exhibits a forward-bias turn-on voltage of 1.68 V with an ideality factor of 2.5. In the reverse direction, the breakdown voltage is 9 V and the leakage current prior to breakdown is lower than 50 μA at 8 V.

Figure 6 shows room-temperature electroluminescence (EL) emission spectra at different forward currents of uncoated orange GaInP LEDs. All the EL emission wavelengths $\lambda$ are located at around 610 nm and shift slightly to longer wavelengths with increasing the injecting current. This is due to the band-gap shrinkage caused by the joule heating. The FWHM value at 20 mA of the orange LEDS is 79 meV (23.6 nm) which is larger than that of 51 meV for the p-n Ga$_{0.3}$In$_{0.7}$P red LEDs ($\lambda=670$ nm) prepared by MOVPE and 55–66 meV for the p-n Ga$_{0.68}$In$_{0.32}$P yellow-green LEDs ($\lambda=584$ nm) prepared by LPE. The
FORWARD: 1 V/div., 10 mA/div.
REVERSE: 5 V/div., 10 mA/div.

FIG. 5. Typical current-voltage (I-V) characteristics measured at room temperature of p-n homostructure Ga0.65In0.35P LEDs. (Forward: 1 V/division, 10 mA/division; reverse: 5 V/division, 10 mA/division).

external quantum efficiency at 20 mA achieved is 0.0153% for the uncoated orange LEDs. The fact that the efficiency is not so high in these devices may be due to (a) the lower carrier concentration and high resistivity of the n-type GaAsP (3 \times 10^{17} \text{ cm}^{-3}) and (b) the misfit dislocations originating from the GaAsP substrate.

IV. CONCLUSIONS

We have demonstrated the feasibility of growing the p-n homostructure Ga0.65In0.35P reproducibly by the LP-MOVPE technique. We have optimized the growth temperatures at 700–740 °C and V/III ratios at 100–200 to obtain good quality Ga0.65In0.35P epitaxial layers. The optimum electron and hole concentrations of Si- and Zn-doping levels by using SiH6 and DMZn sources are near 2 \times 10^{18} and 7 \times 10^{17} \text{ cm}^{-3}, respectively, which exhibit the strongest PL peak intensity. The performance of the LEDs has been investigated by means of I-V, EL, and external quantum efficiency. So far, the results of these LEDs still cannot be compared to those of AlGaInP/Ga0.3In0.7P and AlGaAs/GaAs LEDs, which may be due to the substrate imperfections and low electron concentrations at the surface GaAs0.7P0.3 layer. Further study is required to overcome the problem of increasing the concentration of the surface GaAs0.7P0.3 layer and to fabricate heterostructures such as AlGaInP/GaInP to improve the LED performance.

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