Doping studies of $Ga_{0.5}In_{0.5}P$ organometallic vapor-phase epitaxy

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Undoped $Ga_{0.5}In_{0.5}P$ has been successfully grown by organometallic vapor-phase epitaxy on GaAs substrates with a free-electron concentration of 10^{16} cm^{-3} and a mobility of 1050 cm^2/V s in nominally undoped material. The distribution coefficient of indium in the growth of $Ga_{0.5}In_{0.5}P$ is nearly to unity. Both n- and p-type carrier concentrations of up to 10^{19} cm^{-3} have been obtained in the present study. Diethyltelluride and silane are used as n-type dopants. Dimethylzinc is used as the p-type dopant. Te is a very efficient dopant with a distribution coefficient $k_{Te} = 54$. The photoluminescence (PL) intensity increases with Te doping level to a maximum at $n = 2\times10^{18}$ cm^{-3}. The silicon distribution coefficient is temperature dependent, due to the incomplete pyrolysis of silane at the growth temperature. Si-doped $Ga_{0.5}In_{0.5}P$ has a lower PL efficiency than Te-doped samples and is not strongly correlated with carrier concentration. The incorporation efficiency of Zn is low, with $k_{Zn} = 3.8\times10^{-3}$, due to the high vapor pressure of Zn at the growth temperature. The PL intensity of Zn-doped $Ga_{0.5}In_{0.5}P$ also increases with Zn doping level to a maximum at $p = 2\times10^{18}$ cm^{-3} and is comparable to the optimum Te-doped n-type $Ga_{0.5}In_{0.5}P$. Only a single band-edge PL peak is observed in all cases.

I. INTRODUCTION

$Ga_{0.5}In_{0.5}P$ has a direct band gap of 1.9 eV at room temperature and was predicted to be highly efficient luminescence material more than a decade ago.[1] With its lattice constant matched to that of GaAs substrates, no misfit dislocations will be generated during epitaxial growth. Lattice mismatch was shown by Stringfellow[2] to severely degrade $Ga_xIn_{1-x}P$ material quality. This may be a major cause of low light-emitting-diode (LED) efficiency and short device lifetime. However, $Ga_{0.5}In_{0.5}P$ lattice matched to GaAs may be a more efficient red-light-emitting material than either $GaAs_{1-x}P_x$/GaAs or even $Al_xGa_{1-x}As$/GaAs.[3]

The material system $Ga_{0.5}In_{0.5}P$/GaAs also has other device application potential. For example, $Ga_{0.5}In_{0.5}P$ may be used as a wide gap emitter in a heterostructure bipolar transistor.[4] It is expected to be especially useful since the electron affinities of GaAs and $Ga_{0.5}In_{0.5}P$ are predicted to be nearly equal. As a result, there would be no conduction-band "spike" or barrier at the emitter-base junction. With the advent of optical information systems, such as optical memory, audio and video disk playback systems, laser printers, etc., the demand for short-wavelength visible semiconductor lasers is increasing. Double-heterostructure lasers with $Ga_xIn_{1-x}As_yP_{1-y}$ active layers and $Ga_{0.5}In_{0.5}P$ cladding layers on GaAs substrates are expected to cover the wavelength range[5] 7200–8800 Å and those with $Al_{0.5}In_{0.5}P/(AlGa)_{0.5}In_{0.5}P$/GaAs to cover the range[6] 5800–6800 Å. It may also be possible to cover this range using $Al_{0.5}In_{0.5}P/Ga_{0.5}In_{0.5}P$/GaAs quantum-well structures.[7]

Organometallic vapor-phase epitaxy (OMVPE) has proven to be a versatile production technique for manufacturing GaAs solar cells and field-effect transistors (FET's), and especially $Al_xGa_{1-x}As$/GaAs LED's and lasers. In the past, OMVPE growth of indium compounds was plagued by a parasitic chemical reaction between the source materials.[8] Triethylindium (TEIn) reacts with phosphine (PH_3) or arsine (AsH_3) to form a nonvolatile polymeric liquid, which makes epitaxial growth inefficient, irreproducible, and alloy composition nonuniform.[9] In order to inhibit this chemical reaction, OMVPE growth of In compounds at low pressure, with associated precracking of the PH_3, becomes necessary. Further, introducing N_2 into the reactor to retard the gas-phase reaction is apparently critical to successful growth.

By replacing TEIn with trimethylindium (TMIn), most of the difficulties mentioned above can be avoided. At the University of Utah, we have demonstrated the ability to grow high-quality InP (Ref. 10), $Ga_{0.5}In_{0.5}P$ (Ref. 11), $Ga_{0.47}In_{0.53}As$ (Ref. 12), $(AlGa)_{0.5}In_{0.5}P$ (Ref. 13), and GaInAsSb (Ref. 14) using TMIn. Similar success has been obtained in other laboratories.[15–17] In order to make OMVPE-grown $Ga_{0.5}In_{0.5}P$ useful for optical and electronic device applications, the control of both n- and p-type doping is necessary. In this paper, we present our studies of the n-type dopants Te and Si and the p-type dopant Zn in $Ga_{0.5}In_{0.5}P$.

II. EXPERIMENTAL PROCEDURE

The horizontal SiO_2 reactor has a cross section 2 cm high by 5 cm wide. An ir quartz lamp is used to heat the graphite susceptor. The desired temperature can be reached in less than one minute. Separate inlet tubes for the group-III–group-V reactants are used with no phosphine precracking furnace. The system integrity is checked using an *in situ* hygrometer both at the waste line and at the quartz reactor outlet. The water-vapor content of the system is routinely <0.1 ppm, the detection limit of our Ondyne hygrometer. The reactor is operated at a pressure of 1 atm. Although N_2 was found to be critical in certain reactors to reduce gas-phase reactions,[8,16] no N_2 is used during the growth except for purging associated with the loading and unloading of the substrate. The source materials are solid TMIn held in a

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temperature-controlled bath at 17 °C with a vapor pressure of 1 Torr,[18] liquid trimethylgallium (TMGa) at −12 °C, and phosphine diluted to 10% in H_2. The water-vapor content of phosphine is also measured to be <0.1 ppm. Surface morphology is examined using a high-magnification (1600×) Nomarski interference phase-contrast microscope. Hall-effect measurements are made using the Van der Pauw geometry, with Ohmic contacts formed using indium dots alloyed 1 min at 450 °C in H_2. The photoluminescence (PL) is excited using the 488-nm line of the Ar^+ laser, and the spectra are detected with a Spex 1/2-m spectrometer and a Ge *p-i-n* detector cooled to 77 K.

III. RESULTS AND DISCUSSION

A. Undoped $Ga_{0.5}In_{0.5}P$

We report the growth of $Ga_{0.5}In_{0.5}P$ using the growth conditions listed in Table I. The distribution coefficient of indium, defined as $k = X^s_{In}/X^v_{In}$, is nearly equal to unity, as can be seen from Fig. 1. These data are clear evidence that there is no gas-phase reaction leading to premature depletion of indium.

No GaAs buffer layer is grown in our case. However, in a separate experiment, the GaAs substrate was heated to 650 °C in a PH_3/H_2 ambient for 2 min. After this treatment, the GaP LO-phonon peak was detected by a Raman scattering measurement on the surface. This is similar to the results of Mukai, Yajima, and Shimada[19] for liquid-phase epitaxy (LPE) growth of GaInAsP on GaAs, i.e., the GaAs substrate surface is decomposed by reaction with *P*. Such thermal reactions cause the poor reproducibility of surface morphology for GaInAsP grown on GaAs. This result also supports our early findings that it is difficult to grow high-quality $Ga_{0.5}In_{0.5}P$ on GaAs at substrate temperatures higher than 650 °C.[11] Nevertheless, $Ga_{0.5}In_{0.5}P$ can be grown at higher temperatures if a thin $Ga_{0.5}In_{0.5}P$ buffer layer is grown at lower temperatures to protect the GaAs substrate prior to the high-temperature $Ga_{0.5}In_{0.5}P$ growth, similar to the technique used for $Ga_{0.47}In_{0.53}As$ grown on InP substrates.[12] Under the growth conditions described above and summarized in Table I, epitaxial layers with perfect mirror like surface morphologies can be obtained. When there is a slight lattice mismatch between the epitaxial layer and the substrate, misfit dislocations along the ⟨110⟩ direction are observed. The unintentionally doped $Ga_{0.5}In_{0.5}P$ has a free-electron concentration of 10^{16} cm^{-3} with a mobility of 1050 cm^2/V s. The PL intensity $Ga_{0.5}In_{0.5}P$ is comparable to that of InP grown in the same reactor. The half-width of the room-temperature PL peak is typically 39 meV.

TABLE I. $Ga_xIn_{1-x}P$ growth conditions.

Substrate	GaAs(100)
Growth temperature	600–650 °C
H_2 flow rate through TMIn (17 °C)	150 cm^3/min
H_2 flow rate through TMGa (−12 °C)	3–5 cm^3/min
PH_3 flow rate (10% in H_2)	300 cm^3/min
Total H_2 flow rate	2 liter/min
Growth rate	6 μm/h

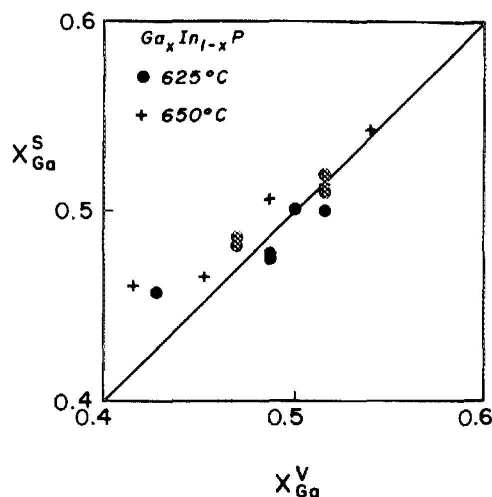

FIG. 1. Solid composition, *x*, for $Ga_xIn_{1-x}P$ vs vapor composition X^v_{Ga} = [TMGa]/[TMIn + TMGa], at 625 °C (●) and 650 °C (+).

B. *n*-type dopants

1. Diethyltelluride

Diethyltelluride (DETe) diluted to 5.45 ppm in H_2 is used as the source for the *n*-type dopant. Figure 2 shows the almost linear relation between the dopant mole fraction in the gas phase and carrier concentrations in the range 10^{17} $cm^{-3} < n < 10^{19}$ cm^{-3}. We define the Te distribution coefficient as $k_{Te} = X^s_{Te}/X^v_{Te}$, where X^s = (concentration of electrons)/(concentration of group-V sites) and X^v = (concentration of group-VI dopant in the vapor)/(concentration of P in the vapor). Since the concentration of group-VI dopant is much smaller than the concentration of P in both the solid and the vapor, we neglect the group-VI concentration in the denominator in calculating both X^s and X^v. We calculate the distribution coefficient to be 54.

The PL intensity of Te-doped $Ga_{0.5}In_{0.5}P$ increases with carrier concentration until $n = 2\times10^{18}$ cm^{-3}, as can be seen from Fig. 3. The half-width increases with increasing

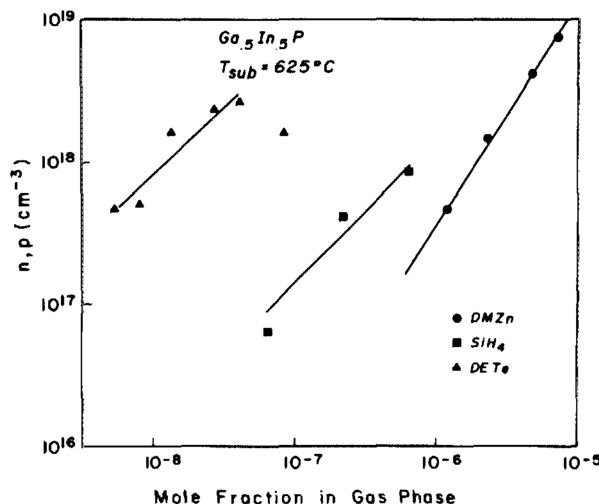

FIG. 2. Carrier concentration as a function of dopant mole fraction in the gas phase at constant PH_3 flow rate and group-V to group-III ratio for Te (▲), Si (■), and Zn (●) doped $Ga_{0.5}In_{0.5}P$.

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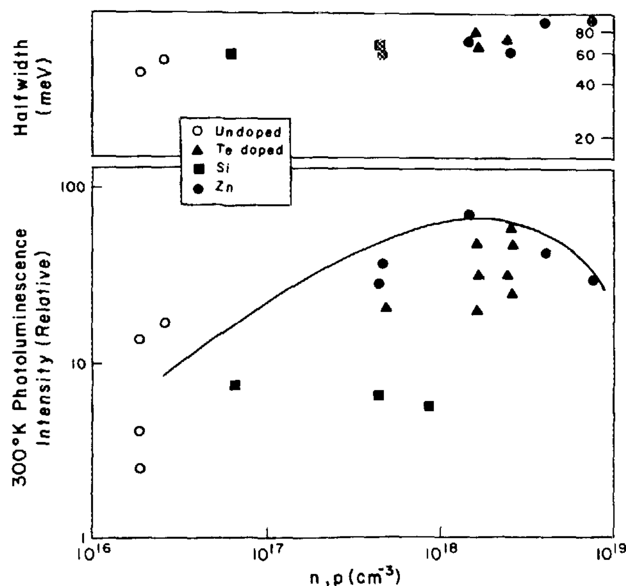

FIG. 3. Relative PL intensity and half-width vs carrier concentration for undoped (O), Te (▲), Si (■), and Zn (●) doped $Ga_{0.5}In_{0.5}P$.

carrier concentration, as shown. The electron mobility of Te-doped $Ga_{0.5}In_{0.5}P$ is shown as a function of doping level in Fig. 4, together with data for undoped and Si-doped $Ga_{0.5}In_{0.5}P$. We see that the electron mobility decreases monotonically from 1020 to 500 $cm^2/V\,s$ as carrier concentration increases from 10^{16} to $10^{19}\,cm^{-3}$, and the curved line represents the best data points.

2. Silane

Several advantages of using Si as the n-type dopant have been reported in the literature:

(1) A sharp doping profile is possible, due to the low Si vapor pressure and low diffusion coefficient at the growth temperature.[20]

(2) Si-doped GaAs was reported to have very high electroluminescence quality.[21]

Silane (SiH_4) diluted to 4.26 ppm in H_2 is used as the dopant source. The carrier concentration is found to be proportional to the silane mole fraction in the gas phase at a growth temperature of 625 °C, as shown in Fig. 2. Doping concentrations as high as $10^{18}\,cm^{-3}$ can be achieved. The Si incorporation efficiency was found, in InP,[22] to be dependent on the silane cracking efficiency. Its temperature dependence was found to be very similar to that of Si-doped[23] GaAs and the Si epitaxial growth rate from silane.[24] The PL measurements of Si-doped $Ga_{0.5}In_{0.5}P$ showed no strong correlation between carrier concentration and PL intensity. The PL was found to be less intense than that for Te-doped $Ga_{0.5}In_{0.5}P$ at comparable carrier concentrations. Both can be seen in Fig. 3. We speculate that the lower PL efficiency in Si-doped material is due to a slight amount of O_2 and/or H_2O in the system which reacts with Si. Similar results were seen in Si-doped InP.[22] Only a single band-edge emission peak around 0.66 μm was found in the wavelength range shorter than 0.87 μm, which corresponds to the GaAs substrate band gap.

C. *p*-type dopant

1. Dimethylzinc

Dimethylzinc (DMZn) is used as a p-type dopant source with a concentration of 474 ppm in H_2. Carrier concentrations in the range $10^{17}\,cm^{-3} < p < 10^{19}\,cm^{-3}$ can be readily obtained by varying the DMZn mole fraction in the gas phase, as shown in Fig. 2. Its superlinear dependence is similar to that of Zn-doped InP.[22] The Zn distribution coefficient, defined as $k_{Zn} = X^s_{Zn}/X^v_{Zn}$, with $X^v_{Zn} = [DMZn]/[TMIn + TMGa]$, is found to be 0.0038 at $p = 10^{18}\,cm^{-3}$ and a growth temperature of 625 °C. This low doping efficiency is due to the fact that Zn has a vapor pressure of 15 Torr at the growth temperature,[25] and most of the zinc is

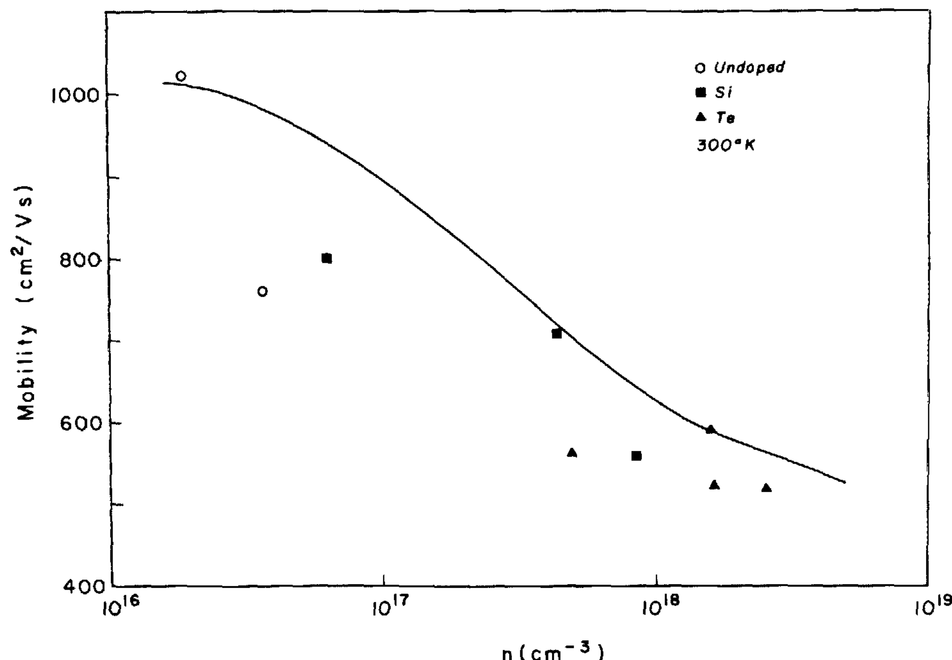

FIG. 4. Room-temperature electron mobility as a function of carrier concentration for undoped (O), Te (▲), and Si (■) doped $Ga_{0.5}In_{0.5}P$.

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evaporated from the crystal surface before incorporation. Samples intentionally DMZn doped at $<10^{17}$ cm^{-3} are n type. From results[22] on InP we estimate the total impurity concentration to be in the range 10^{16}–10^{17} cm^{-3}. Thus, controlled p-type doping below this level is difficult.

$Ga_{0.5}In_{0.5}P$ hole mobilities are in the range of 20–40 cm^2/V s. PL measurements of Zn-doped $Ga_{0.5}In_{0.5}P$ show only a single near-band-edge emission peak with no deep-level ir peak observed. This is quite different than the results for InP, where Zn doping produced a broad deep-level luminescence peak at 1.16 μm,[22] in addition to the band-edge peak. The room-temperature PL intensity increases with carrier concentration, as shown in Fig. 3; quenching set in at $p = 2\times 10^{18}$ cm^{-3}. The maximum PL intensity for p-type $Ga_{0.5}In_{0.5}P$ is about the same as that of n-type samples. This differs from early observations for InP, where the n-type PL intensity is 10–100 times stronger than that of p-type material.[22,26] Also shown in Fig. 3 is the half-width, which increases at higher concentrations, as expected.

IV. CONCLUSIONS

In summary, undoped $Ga_{0.5}In_{0.5}P$ was successfully grown on GaAs substrates with $n = 10^{16}$ cm^{-3}, $\mu = 1050$ cm^2/V s, and strong room-temperature PL with a narrow half-width of 39 meV. Surface conversion of GaAs substrates to GaP was detected after exposure PH_3 at substrate temperatures of >650 °C. This is believed to be the major case of poor growth morphology for $Ga_{0.5}In_{0.5}P$ grown at higher temperatures. DETe and silane were used as n-type dopants. Te has a high distribution coefficient, with $k_{Te} = 54$. The PL intensity of Te-doped $Ga_{0.5}In_{0.5}P$ increases with carrier concentration for $n < 2\times 10^{18}$ cm^{-3}, after which quenching sets in. Si has a temperature-dependent distribution coefficient, due to the temperature-dependent silane cracking efficiency. Si-doped $Ga_{0.5}In_{0.5}P$ has lower PL intensities than Te-doped materials. The PL intensity is not strongly correlated with carrier concentration. DMZn is used as the p-type dopant. Despite its low incorporation efficiency, $k_{Zn} = 3.8\times 10^{-3}$, carrier concentrations as high as $p = 10^{19}$ cm^{-3} were achieved at suitable flow rates. The maximum PL intensity occurs at $p = 2\times 10^{18}$ cm^{-3} and is as strong as that of optimally doped n-type $Ga_{0.5}In_{0.5}P$. There is no observable deep-level related luminescence for any dopant studied.

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