Heavy Be doping of GaP and $In_xGa_{1-x}P$

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Very high p-type doping is achieved in GaP and $In_xGa_{1-x}P$ with Be in solid source molecular beam epitaxy equipped with a valved phosphorus cracker. Dependence of hole concentration on the growth temperature and on the Be flux during growth is studied for GaP. The hole concentration peaks at 3×10^{19} cm^{-3} for normal temperature (600 °C) growth. It is slightly higher at a lower growth temperature of 400 °C for the same Be flux. A higher hole concentration (5×10^{19} cm^{-3}) is obtained by giving a high temperature rapid thermal anneal to this sample. A hole concentration of 2×10^{19} cm^{-3} is achieved in $In_{0.49}Ga_{0.51}P$ by using a lower temperature growth (350 °C). To our knowledge, this is the highest reported hole concentration for any p-type dopant in $In_{0.49}Ga_{0.51}P$. *© 1996 American Vacuum Society.*

I. INTRODUCTION

There has been an increased interest in the quaternary $(Al_xGa_{1-x})_yIn_{1-y}P$ in recent years because it gives a direct band gap up to 2.2 eV and is thus an attractive material system for visible optoelectronic devices. Efficient light emitting diodes (LEDs) from red to green region were recently reported.[1,2] However, achieving high p-type doping in this system has been difficult.[3,4] This results in increased contact resistance for nonalloyed contacts. Also, the low p-type doping efficiency contributes to a high series resistance which can limit the performance in high current density devices like laser diodes.

Various dopants like carbon, zinc, magnesium, and beryllium are used for the p-type doping of this compound semiconductor. Fairly high hole concentrations were reported using carbon—in excess of 1×10^{20} cm^{-3} in GaP films grown by metalorganic molecular beam epitaxy (MOMBE)[5] and 5×10^{18} cm^{-3} for $In_{0.5}Ga_{0.5}P$ epilayers grown by gas-source molecular beam epitaxy (GSMBE).[6] However, heavy carbon doping is believed to reduce minority carrier lifetime in GaAs LEDs.[7] Hence it is desirable to use some other p-type dopant for these minority carrier devices. The hole concentration of Zn doped $In_{0.5}Ga_{0.5}P$ saturated near 10^{18} cm^{-3} for samples grown by both atmospheric pressure[4] and low pressure[3] metalorganic chemical vapor deposition (MOCVD). Similar results were obtained for magnesium in chemical beam epitaxy (CBE).[8] Obtaining very high p-type doping with beryllium was also difficult for $In_xGa_{1-x}P$ LEDs grown by GSMBE.[9] Be in solid source molecular beam epitaxy (MBE) was reported to give 3×10^{18} cm^{-3} holes.[10] In this article, we report the beryllium doping characteristics in GaP and $In_xGa_{1-x}P$ layers grown by solid source MBE using a valved phosphorus cracker.

II. EXPERIMENTAL DETAILS

All the samples used in this study were grown in a modified Varian GEN-II CBE system. A valved cracker source was used for phosphorus source. Temperature was monitored with a thermocouple. Composition and growth rate were calibrated using reflection high energy electron diffraction (RHEED) intensity oscillations. The details of growth were reported elsewhere.[11] Be doped GaP epilayers were grown on GaP(100) substrates. $In_xGa_{1-x}P$ ($x\neq0.49$) was grown lattice mismatched on GaP using a linearly graded buffer layer.[9] $In_{0.49}Ga_{0.51}P$ was grown lattice matched on GaAs(100) substrate. The nominal growth rate was 1 μm/h for all the samples. Van der Pauw Hall measurements were done to find the hole concentration. In–Zn alloyed contacts were used at the four corners of rectangle shaped samples.

III. RESULTS AND DISCUSSION

An approach similar to Be doping in GaAs was used during these experiments.[12] Be in GaAs is an amphoteric dopant. It has been reported that in GaAs very high hole concentrations can be achieved using Be by growing the film at a low temperature and then annealing it at a higher temperature.[12] This drives the interstitial Be (donor) onto acceptor (Ga) sites. Similarly, the ratio of Be atoms on acceptor sites to Be atoms on donor sites for GaP could be written as[12]

$$\frac{N_A^-}{N_D^+}=\left(\frac{n_i}{p}\right)^2[K'(T)(P_{P_2})^{0.5}],\tag{1}$$

where (P_{P_2}) is the partial pressure of phosphorus dimer, $K'(T)$ is a temperature dependent constant, n_i is the intrinsic carrier concentration and p is the hole concentration. It has been shown that low temperature growth of GaP results in excess phosphorus.[13] A subsequent anneal at a high temperature increases both n_i and P_p, which can help to increase the hole concentration. Be doping efficiency (ratio of hole concentration to the Be concentration) was investigated as a

TABLE I. Dependence of hole concentration on growth temperature in GaP. For all the films, Be flux was set at 1×10^{20} cm^{-3}. The anneal was a rapid thermal anneal at 900 °C for 30 s.

Growth temp. (°C)	As grown hole conc. (cm^{-3})	As grown mobility (cm^2/V s)	After anneal hole conc. (cm^{-3})	After anneal mobility (cm^2/V s)
300	Resistive	⋯	Resistive	⋯
350	Resistive	⋯	Resistive	⋯
400	3.9×10^{19}	27	4.9×10^{19}	26
600	1.27×10^{19}	36	1.97×10^{19}	35

TABLE II. Be doping results in $In_xGa_{1-x}P$.

Film composition	T_{growth} (°C)	Be flux (cm^{-3})	p (cm^{-3})
$In_{0.3}Ga_{0.7}P$	560	1×10^{19}	9.1×10^{18}
$In_{0.49}Ga_{0.51}P$	530	1×10^{20}	3.5×10^{18}
$In_{0.49}Ga_{0.51}P$	350	1×10^{20}	2.6×10^{19}
$In_{0.55}Ga_{0.45}P$	520	3×10^{19}	2.6×10^{19}

function of substrate temperature during growth for GaP. For various substrate temperatures, Be flux was set for 1×10^{20} cm^{-3} at 1 ML/s growth rate. Films grown at 300 and 350 °C were highly resistive as grown. 400 °C growth resulted in a hole concentration of 3.9×10^{19} cm^{-3} and 600 °C grown films showed 1.3×10^{19} cm^{-3} holes. These results are summarized in Table I.

A similar experiment was done for $In_{0.49}Ga_{0.51}P$ grown lattice matched on GaAs. For this, the normal growth temperature is 530 °C. Two epilayers were grown at 350 and 530 °C with Be set to incorporate 1×10^{20} cm^{-3} holes. The 530 °C growth resulted in 3.5×10^{18} cm^{-3} holes. A dramatic increase was seen for the 350 °C grown film, which showed hole concentration of 2.6×10^{19} cm^{-3}. These results are summarized in Table II.

All GaP films were given a 900 °C, 30 s rapid thermal anneal to see the effect of n_i. In GaP, the n_i values at 600 and at 900 °C are 2.2×10^{13} and 1.6×10^{15} cm^{-3} respectively, thus giving two orders of magnitude increase in n_i. After anneal, the 300 and 350 °C grown films still stayed resistive. In the 400 °C grown film hole concentration increased to 4.9×10^{19} cm^{-3} and in 600 °C, it increased to 2×10^{19} cm^{-3}. (Table I). These results are discussed at the end.

While investigating the effect of growth temperature on hole concentration in GaP, it was observed that 1×10^{20} cm^{-3} of Be resulted in only about 1.3×10^{19} cm^{-3} holes for the 600 °C growth. In the second set of experiments, samples were grown at 600 °C with different Be fluxes. The results are shown in Fig. 1. The doping efficiency is unity till Be concentration of about 3×10^{19} cm^{-3} and then it falls down rapidly.

All these doping results obtained for GaP are consistent with an amphoteric behavior of Be in GaP. From the 400 and 600 °C results in Table I, it can be seen that the excess phosphorus partial pressure during low temperature growth increases the hole concentration (the as-grown results). During the high temperature anneal, hole concentrations in both the samples are increased, indicating the effect of n_i suggested by Eq. (1). The hole concentration dependence on Be flux (Fig. 1) also points to Be as an amphoteric dopant. When moderate amounts of Be (upto 3×10^{19} cm^{-3}) are put in, all of it goes on acceptor sites (unity doping efficiency). But for higher Be fluxes (equivalent to 1×10^{20} cm^{-3}), we speculate that the excess Be goes into interstitial sites. The interstitial Be is a deep donor and it compensates the acceptors, thus reducing the net hole concentration. In these experiments, Be incorporation into the film is believed to be 100%, similar to Be incorporation in GaAs. Further secondary ion mass spectroscopy studies would clarify this.

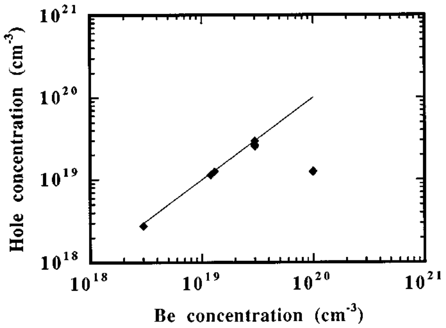

FIG. 1. Dependence of hole concentration on Be concentration for normal temperature (600 °C) growth in GaP. The straight line represents unity doping efficiency of Be.

IV. CONCLUSION

In conclusion, we report very high p doping in GaP and $In_xGa_{1-x}P$ using a valved phosphorus cracker source in MBE. Using a combination of low temperature growth followed by an *ex situ* rapid thermal anneal, a hole concentration of 5×10^{19} cm^{-3} is achieved in GaP. These results are consistent with the amphoteric nature of Be. For $In_{0.49}Ga_{0.51}P$, low temperature growth results in a very high hole concentration of 2.6×10^{19} cm^{-3}.

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