Nonalloyed ohmic contacts to heavily Be-doped GaP and $In_xGa_{1-x}P$

M. V. Tagare, T. P. Chin, and J. M. Woodall
School of Electrical and Computer Engineering and NSF-MRSE Center for Technology Enabling Heterostructure Materials, Purdue University, West Lafayette, Indiana 47907-1285

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Nonalloyed ohmic contacts, with contact resistances as low as 9 $\mu\Omega$ cm^2, are obtained to p^{++} GaP using Ni and Ti–Au. Very high *p*-type doping (5×10^{19} cm^{-3}) is achieved in GaP using a growth temperature of 400 °C followed by an *ex situ* high-temperature rapid thermal anneal. The *p*-type dopant is beryllium and the films are grown by solid source molecular beam epitaxy equipped with a valved phosphorus cracker. A record high hole concentration (2×10^{19} cm^{-3}) is reported in $In_{0.49}Ga_{0.51}P$ by using a growth temperature of 350 °C. © *1996 American Institute of Physics.* [S0003-6951(96)03924-1]

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.[1,2] For efficient and reliable operation of these devices, it is essential to use the lowest resistance ohmic contacts possible. Various metals have been used for *p*-type contacts to GaP and $In_xGa_{1-x}P$.

Ohmic Au–Zn contacts have been obtained to *p*-type GaP after a heat treatment at 600 °C for 2 min.[3] The specific contact resistance (ρ_c) was 6.5×10^{-4} Ω cm^2. Also, the Au–Be eutectic and Au–Be–Ni alloy were used for making ohmic contacts to *p*-type GaP.[4] The optimal sintering temperature for these contacts was between 450 and 570 °C in hydrogen ambient for 2 min. The lowest ρ_c was 7.5×10^{-5} Ω cm^2. Alloyed Au–Zn contacts were also used for *p*-type $In_{0.26}Ga_{0.74}P$[5] ($\rho_c=3\times10^{-3}$ Ω cm^2). Since high-temperature heat treatment is required to get good alloyed ohmic contacts, they cannot serve as good reflectors.

The limiting factor in getting good nonalloyed ohmic contacts to *p*-type material in this system is the difficulty in achieving high *p*-type doping.[6,7] Hole concentrations in excess of 1×10^{20} cm^{-3} in GaP films[8] and 5×10^{18} cm^{-3} for $In_{0.5}Ga_{0.5}P$ epilayers[9] were reported using carbon. However, heavy carbon doping is believed to reduce minority carrier lifetime in GaAs light-emitting diodes (LEDs).[10] Hence it is desirable to use some other *p*-type dopant for these minority carrier devices. The highest hole concentrations achieved using group II dopants such as zinc,[6,7] magnesium,[11] and beryllium[12] and various growth techniques have been around 10^{18} cm^{-3}.

In this letter we report low resistance (9×10^{-6} Ω cm^2) nonalloyed ohmic contacts to heavily doped *p*-type GaP. We are able to achieve hole concentrations as high as 5×10^{19} cm^{-3} in GaP by growing the films at lower temperatures than normal, followed by a high-temperature rapid thermal anneal. For $In_{0.49}Ga_{0.51}P$ we obtained a hole concentration of 2.6×10^{19} cm^{-3} by a low-temperature growth. The details of these doping studies are reported elsewhere.[13] Nonalloyed ohmic contacts are also obtained using Ni on $In_xGa_{1-x}P$.

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.[14] Composition and growth rate were calibrated using reflection high-energy electron diffraction (RHEED) oscillations. A thermocouple was used to monitor the temperature. The details of growth were reported elsewhere.[15] Be-doped GaP and $In_{0.49}Ga_{0.51}P$ epilayers were grown on GaP(100) and GaAs(100) substrates, respectively. $In_xGa_{1-x}P$ ($x\neq0.49$) was grown lattice mismatched on GaP(100) substrates using a linearly graded buffer layer.[5] The nominal growth rate was 1 μm/h for all the samples.

The doping studies indicated that Be behaves like an amphoteric dopant in GaP. The ratio of Be atoms on acceptor sites to Be atoms on donor sites for GaP can be written as[16]

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

where (P_{P_2}) is the partial pressure of the phosphorus dimer, $K'(T)$ is a temperature-dependent constant, n_i is the intrinsic carrier concentration, and p is the hole concentration. Low-temperature growth of GaP results in excess phosphorus.[17] A subsequent anneal at a high temperature increases both n_i and the partial pressure of phosphorus, which can help to increase the hole concentration. The high-temperature anneal drives the interstitial Be (donor) onto acceptor (Ga) sites. For films grown at 400 and 600 °C (normal growth temperature) with Be flux set for 1×10^{20} cm^{-3} at 1 ML/s growth rate the hole concentrations are 3.9×10^{19} cm^{-3} and 1.3×10^{19} cm^{-3}, respectively (Table I). An *ex situ* rapid thermal anneal of 900 °C for 30 s to these samples results in increased hole concentrations of 4.9×10^{19} cm^{-3} and 1.97×10^{19} cm^{-3}, respectively. The hole concentration is also dependent on the Be flux during growth. The doping efficiency is unity until Be concentration of about 3×10^{19} cm^{-3} and then it decreases rapidly.

TABLE I. Dependence of hole concentration on growth temperature in GaP. For all the films, Be flux was set for 1×10^{20} cm^{-3} holes. 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. Summary of alloyed and nonalloyed contacts on *p*-type GaP. The first film was grown at 400 °C and given an *ex situ* rapid thermal anneal at 900 °C for 30 s. Be (cm^{-3}) gives the estimated Be atoms incorporated into the film.

Hole conc. (cm^{-3})	^{T}growth (°C)	Be (cm^{-3})	Metal used	Alloying condition	ρ_c (Ω cm^2)
5×10^{19}	400 (+ anneal)	1×10^{20}	Ti–Au	Nonalloyed	8.9×10^{-6}
3×10^{19}	600	3×10^{19}	Au–Zn(3%)	450 °C, 90 s	4.3×10^{-5}
			Ni–Ti–Au	Nonalloyed	2.9×10^{-4}
			Ti–Au	Nonalloyed	1.4×10^{-4}
3×10^{18}	600	3×10^{18}	Au–Zn(3%)	450 °C, 90 s	1×10^{-4}
			Ni–Ti–Au	Nonalloyed	9×10^{-2}
			Ti–Au	Nonalloyed	Nonohmic

All these results point to Be being an amphoteric dopant. An increased hole concentration is obtained by a lower growth temperature and by an *ex situ* high-temperature anneal as suggested by Eq. (1). The hole concentration dependence on the Be flux during growth can be explained as due to the excess Be (interstitial donor) compensating the acceptors, thus reducing the net hole concentration.

For the study of various contacts on *p*-type GaP and $In_xGa_{1-x}P$, the electrical properties of alloyed Au–Zn contacts were used as the baseline. *P*-type GaP epilayers with hole concentrations 3×10^{18} and 3×10^{19} cm^{-3} were studied. Both the films were grown at normal temperature with hole concentrations of 3×10^{18} and 3×10^{19} cm^{-3}, respectively. Au–Zn(3%) alloy was thermally evaporated onto the samples. The contacts were annealed at 450 °C for 90 s in nitrogen ambient. The specific contact resistance (ρ_c) was calculated using the transmission line method.[18] The lowest ρ_c obtained during these experiments is 4.3×10^{-5} Ω cm^2 (Table II). E-beam evaporated Ni and Ti–Au were used for nonalloyed contacts. For the 3×10^{19} cm^{-3} doped sample, both contacts are ohmic, with ρ_c in the range 1×10^{-4} Ω cm^2. For the 3×10^{18} cm^{-3} doped sample, the Ti–Au contact exhibits nonohmic behavior and the Ni contacts show a substantially higher (9×10^{-2} Ω cm^2) contact resistance. Ti–Au was also deposited on the 5×10^{19} cm^{-3} doped GaP film. This film was grown at 400 °C with target Be of 1×10^{20} cm^{-3} and then annealed at 900 °C for 30 s. The ρ_c for these contacts is 8.9×10^{-6} Ω cm^2. To our knowledge, this ρ_c is the lowest reported to date.

To determine the electron transport mechanism, temperature-dependent $I-V$s were taken for the Ni contacts. The $I-V$ remains unchanged from its room-temperature curve for temperatures as low as 77 °K. It has been shown[19] that, to the first order, the contact resistance for tunneling contacts is independent of temperature. Since this is what is observed experimentally, it can be concluded that the contacts are of the tunneling type. The contact resistance for 5×10^{19} cm^{-3} doped film is 8.9×10^{-6} Ω cm^2 compared to 2.9×10^{-4} Ω cm^2 for 3×10^{19} cm^{-3} doping. This is also in agreement with the strong dependence of contact resistance of tunneling contacts on doping.

Another point should be noted. It can be seen from Table II that the contact resistances for Ni and Ti were comparable for the 3×10^{19} cm^{-3} doped film. The work functions (Φ_m) of these two metals differ by about 1 eV. The comparable ρ_c, in spite of this significant difference in Φ_m, indicates that Φ_{B_p}, the barrier height on p^{++}GaP, might be the same for both these metals. This in turn suggests that the surface Fermi level in p^{++}GaP could be pinned.

Table III summarizes the doping experiments for $In_xGa_{1-x}P$. For $In_{0.49}Ga_{0.51}P$, a dramatic increase in hole concentration (2.6×10^{19} cm^{-3}) was seen at a growth temperature of 350 °C compared to 530 °C (3.5×10^{18} cm^{-3}) with the Be flux set for 1×10^{20} cm^{-3}. However, for $In_{0.55}Ga_{0.45}P$ (only 6% more In) and for $In_{0.3}Ga_{0.7}P$, 2×10^{19} cm^{-3} holes were obtained at normal growth temperature by setting the Be flux for 2×10^{19} cm^{-3}. These results are very similar to the hole concentration dependence on Be flux in GaP, suggesting an amphoteric nature of Be in $In_xGa_{1-x}P$ also.

Nonalloyed ohmic contacts with ρ_c between 1×10^{-2} and 7×10^{-4} Ω cm^2 are obtained on these $In_xGa_{1-x}P$ films using Ni (Table III). For normal temperature grown films with comparable hole concentrations, the contact resistance is found to be an order of magnitude lower for $In_{0.3}Ga_{0.7}P$ compared to $In_{0.55}Ga_{0.45}P$. This difference could be related to the increasing barrier height in this alloy with increasing In fraction.[20] However, for the low-temperature grown $In_{0.49}Ga_{0.51}P$, ρ_c was lower than that for $In_{0.3}Ga_{0.7}P$. Clearly, more experiments are needed on these contacts and are being done. The data on contact resistance to 3.5×10^{18} cm^{-3}

TABLE III. Summary of doping and contacts for *p*-type $In_xGa_{1-x}P$. Be concentration corresponds to the estimated Be atoms incorporated into the film.

Film composition	^{T}growth (°C)	Be conc. (cm^{-3})	Hole conc. (cm^{-3})	Metal used	Alloying condition	ρ_c(Ω cm^2)
$In_{0.3}Ga_{0.7}P$	560	1×10^{19}	9.1×10^{18}	Au–Zn(3%)	450 °C, 90 s	5.8×10^{-4}
$In_{0.3}Ga_{0.7}P$	560	2×10^{19}	1.8×10^{19}	Ni–Ti–Au	Nonalloyed	3.1×10^{-3}
$In_{0.49}Ga_{0.51}P$	350	1×10^{20}	2.6×10^{19}	Ni–Ti–Au	Nonalloyed	7.5×10^{-4}
$In_{0.49}Ga_{0.51}P$	530	1×10^{20}	3.5×10^{18}	…	…	…
$In_{0.55}Ga_{0.45}P$	520	3×10^{19}	2.6×10^{19}	Ni–Ti–Au	Nonalloyed	1×10^{-2}

doped $In_{0.49}Ga_{0.51}P$ is not available at present.

In conclusion, low resistance (9×10^{-6} Ω cm^2) nonalloyed tunneling ohmic contacts to heavily doped *p*-type GaP are reported. Hole concentrations as high as 5×10^{19} cm^{-3} are achieved in GaP by using a low-temperature growth followed by a high-temperature rapid thermal anneal. Nonalloyed ohmic contacts are also obtained on *p*-type $In_xGa_{1-x}P$. For $In_{0.49}Ga_{0.51}P$ hole concentration of 2.6×10^{19} cm^{-3} is obtained by a low-temperature growth.

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