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Electrical and optical properties of undoped InP grown at low temperature by atomic layer molecular beam epitaxy

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The electrical and optical properties of undoped InP layers grown at low temperatures by solid source atomic layer molecular beam epitaxy are investigated. Phosphorus surface coverage during epitaxy is controlled by monitoring the evolution of reflection high-energy electron diffraction pattern during growth. An accurate phosphorus supply by means of a valved cracking phosphorus cell is employed. The relation between phosphorus incorporation and the electronic properties of the epilayers is examined, and it is found that, at a substrate temperature of 340 °C, residual electron concentration increases linearly with phosphorus flux. Residual doping of InP layers grown at 340 °C has been reduced down to 1×10^{16} cm^{-3}, and Hall mobilities of 3260 cm^2/V s at 300 K and 14 830 cm^2/V s at 65 K are reported. Low-temperature photoluminescence of low background doping layers is dominated by near band transitions. © *1995 American Institute of Physics.*

Growth of InP at low substrate temperature is interesting for many reasons. It permits a more efficient phosphorus incorporation during growth which means a low beam equivalent pressure (BEP) of P_2 ($<10^{-5}$ mb), adequate for UHV techniques as molecular beam epitaxy (MBE).[1] In particular, atomic layer molecular beam epitaxy (ALMBE) at low temperatures is a suitable technique to grow abrupt interfaces and doping profiles with low dopant diffusion. Also it is appropriate to the growth of pseudoquaternary alloys of the type $Ga_xIn_{1-x}As_yP_{1-y}$ using (InP)/($Ga_{0.47}In_{0.53}As$) short-period superlattices, avoiding P and As competition, showing excellent structural and optical properties in optoelectronic devices.[2] Finally, it is possible to apply it to the monolithic integration of these devices and others based on InP and related compounds with CMOS-Si circuits.[3] But low temperature grown InP, either by gas source molecular beam epitaxy (GSMBE)[4] or by migration enhanced epitaxy (MEE)[5] using InP as phosphorus source, shows a high-level n-type residual doping which increases dramatically with decreasing growth temperature; residual donors have been identified as a stoichiometry-related native defect in InP,[4,5] related to excessive incorporation of phosphorus. Photoluminescence from these low temperature grown layers is dominated by deep centers killing band-edge emission.[6] Recently we have demonstrated how to reduce the residual doping of InP epilayers grown at substrate temperature of 275–340 °C by more than an order of magnitude as compared to other low temperature grown InP layers. We have used a new technique, solid source atomic layer molecular beam epitaxy (ALMBE) with a control of the phosphorus pulses supplied by a valved cracking cell.[7] In this work, the role of phosphorus incorporation on the electrical and optical properties of undoped layers grown at 340 °C are investigated by means of variable temperature Hall measurements and low-temperature photoluminescence.

The layers were grown on Fe-doped (100) InP substrates by ALMBE in a standard MBE system except for the As and P effusion cells, which are specially designed to operate in a pulsed mode by incorporating a fast-acting valve.[8] The P cell incorporates a cracking section to provide P_2 pulses of perfect rectangular profile and reproducible and controlled amplitude. In ALMBE only group V element is modulated. If τ is the time needed to deposit one monolayer of InP, determined by reflection high-energy electron diffraction (RHEED) oscillations during growth by conventional MBE at 420 °C, with a BEP of $P_2 \sim 4-5\times10^{-6}$ mb, the phosphorus valve is open a fraction of τ just after an In stabilized surface has been reached. The duration of P_2 supply is sufficient to complete one monolayer, and substrate temperature should be as low as possible to avoid phosphorus desorption. In supply per period has been adjusted to an atomic layer in the (100) InP plane. Layers were grown at 340 °C. The pulse amplitude BEP was varied in the range $0.6-4\times10^{-6}$ mb, and pulse length was 0.6τ s at each monolayer. Growth rate and layer thicknesses were 1 monolayer per second and 2 μm, respectively. We have monitorized surface reconstruction by RHEED during the growth, and using growth conditions optimized to reduce residual doping, we have observed that diffraction pattern alternates from P stabilized (2×1), during the P_2 pulse, to In stabilized (2×4) shortly after P_2 is turned off. At 340 °C this point is reached with P_2 pulse amplitudes in the range $0.8-1.5\times10^{-6}$ mb. For higher or lower values of phosphorus pressure, clear (2×1) or (2×4) RHEED pattern were observed during the whole period. Residual n-type doping is shown in Fig. 1 as a function of pulse amplitude. This residual doping, which have been attributed to an excess phosphorus incorporation,[4,5] increases linearly with phosphorus pressure in the pulses.

Figure 2 shows electron concentration as a function of $1/T$ for five undoped samples grown at various phosphorus pressures. At low temperature data depart from the behavior typical of an impurity ionization process, by showing a strong nonlinear behavior versus $1/T$ in the low-temperature range. A similar behavior has been observed in GaAs[9] with n (300 K)$=1\times10^{14}$ cm^{-3} as well as in liquid phase epitaxy grown InP[10] with n (300 K)$=1.6\times10^{16}$ cm^{-3}, and has been attributed to two-band conduction involving the conduction band and a impurity band. Although it is obvious that for two bands conduction Hall coefficient measurements do not simply supply carrier concentrations as for one band, we have

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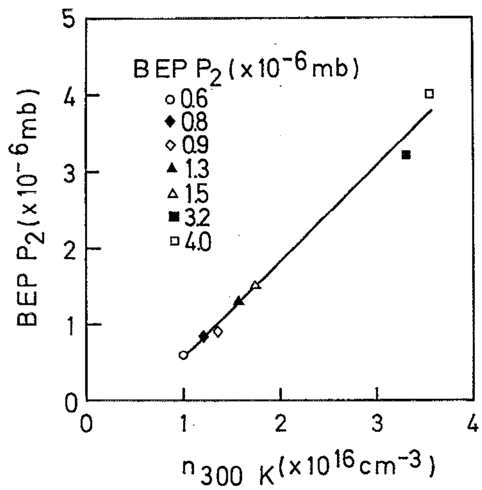

FIG. 1. Room-temperature electron concentration of intentionally undoped InP versus amplitude of phosphorus pulse (beam equivalent pressure). Substrate temperature was 340 °C, phosphorus pulse length 0.6 s, and growth rate of 1 monolayer per second.

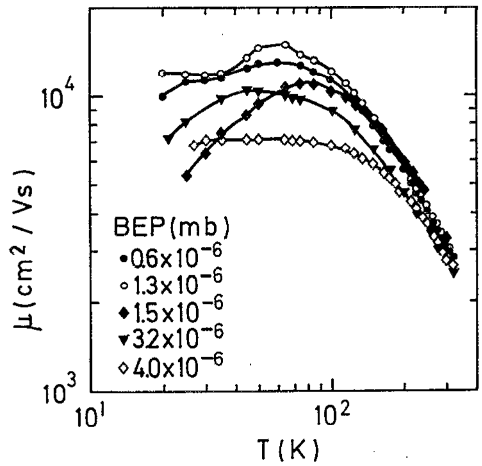

FIG. 3. Temperature dependence of Hall mobility of samples of Fig. 2.

employed usual Hall data versus $1/T$ as a first-order approximation to obtain donor activation energy. In this way an activation donor energy of the order of 15 meV has been found, similar to the value (14.3 meV) found in Ref. 5. This value is somewhat higher than the corresponding one for Si or S (7 meV) residual impurities, typical for high temperature grown InP, and much lower than the 320 meV found in InP grown at low temperatures by gas source MBE.[4]

Maximum Hall mobilities of 3260 cm^2/V s at 300 K and 14 830 cm^2/V s at 65 K were recorded for a sample with room-temperature carrier concentration of 1×10^{16} cm^{-3}, which was grown with a phosphorus pulse amplitude of 1.3×10^{-6} mb. Those values are higher than those found in InP grown by chemical beam epitaxy (Sudersena *et al.*)[11] with their lowest growth temperature of 450 °C; they have observed that the free-carrier concentration n decreases and mobility μ increases with increasing growth temperature in the 450–530 °C range. They obtain InP layers grown at 450 °C with mobilities of 7500 cm^2/V s at 77 K for a carrier concentration $n=1\times10^{16}$ cm^{-3}. When they increase the growth temperature up to 500 °C they found the highest mobilities which have been obtained for an InP epilayer by any molecular beam technique.

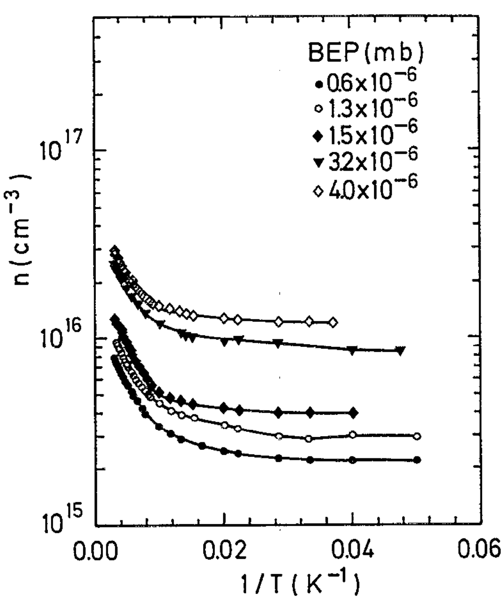

FIG. 2. Temperature dependence of carrier concentration for samples of Fig. 1.

Figure 3 shows the dependence of electron mobility upon temperature for the samples of Fig. 2. In the high-temperature region, for sample with n (300 K)$=1\times10^{16}$ cm^{-3}, mobility follows a temperature dependence of the form $T^{-1.4}$. The value of this exponent is typical for doped InP, where mobility is limited by optical phonon scattering processes, and decreases with increasing carrier concentrations. A maximum mobility is observed near 70 K, below these temperatures all samples exhibit a dominance of ionized-impurity scattering. The peak value increases with decreasing phosphorus pressure, that is, with decreasing electron concentration. For a set of samples grown with P_2 BEP lower than 0.5×10^{-6} mb, we have observed a degradation of the mobility which can be attributed to the presence of another kind of mobility limiting stoichiometric defects, perhaps phosphorus vacancies.

Optical quality of the samples was checked by low-temperature photoluminescence. Figure 4 shows 10 K spectra for the three layers with different BEP of P_2 values: 1.3×10^{-6}, 1.5×10^{-6}, and 3.2×10^{-6} mb. A near band transition centered at 1.412 eV dominates the spectrum of the layer grown under a phosphorus pressure of 1.3×10^{-6} mb. However, for increasing phosphorus pressure, the dominant transition shifts towards lower energies. Spectrum for layer grown with P_2 BEP of 3.2×10^{-6} mb is dominated by a peak centered around 1.395 eV, which has been identified as an exciton bound to deep levels.[12] This defect-induced bound exciton has been previously observed in annealed,[13,14] ion-implanted,[15] or heavily electron irradiated[16] InP, as well as in epitaxial InP.[17,18]

In summary, the growth of InP layers at low temperature

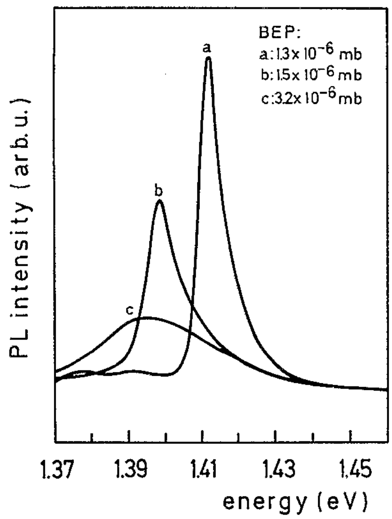

FIG. 4. Photoluminescence spectra for three residual doping InP layers grown with different values of beam equivalent pressure.

by solid source ALMBE is reported. Close control of phosphorus pulse is achieved by means of a valved cracking cell, which is necessary to avoid excess phosphorus incorporation when growing at low substrate temperature. Phosphorus surface coverage by low BEP of P_2 ($\sim 1.0\times 10^{-6}$ mb) is monitored by RHEED pattern recording during growth. InP layers exhibit good electrical and optical quality, with residual doping down to 1×10^{16} cm^{-3}, the lowest value reported for low temperature grown InP.

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