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# Zinc doping of $Ga_{0.51}In_{0.49}P$ grown on GaAs(100) substrates by chemical beam epitaxy

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We report on the *p*-type doping of $Ga_{0.51}In_{0.49}P$ lattice matched to GaAs(100) using gaseous diethylzinc by chemical beam epitaxy. The doping concentration was found to decrease with substrate temperature with an apparent activation energy of 5.3 eV. It was found necessary to keep the substrate temperature below about 500 °C to obtain doping in the $10^{18}/cm^3$ range. The doping concentration shows a 0.8th power law with increasing dopant flow rate and saturates at approximately $5\times10^{18}/cm^3$. The *p*-doped GaInP layers were used as cladding layers for 0.98 $\mu$m strained InGaAs/GaAs lasers which show state-of-the-art performance.

A promising alternative to AlGaAs as a wide band-gap material is $Ga_{0.51}In_{0.49}P$ lattice matched to GaAs substrates. The significant advantages of GaInP include low deep level concentrations,[1] a large valence band discontinuity, and a lower reactivity with carbon and oxygen than AlGaAs. Very low recombination velocities ($<1.5$ cm/s) have been reported at the GaInP/GaAs interface.[2] These advantages make GaInP a very attractive material for lasers. The large $\Delta E_v$ makes it suitable for heterojunction bipolar transistor applications without the need for compositionally graded wide band-gap emitters, and the large $\Delta E_c$ (0.2 eV) and $\Delta E_v$ (0.285 eV)[3] make it suitable for complementary device applications. The successful growth of lasers is critically dependent on the ability to achieve sufficiently high ($\sim10^{18}/cm^3$) levels of *n*- and *p*-type doping. While both *n*- and *p*-type doping of GaInP has been reported by metalorganic chemical vapor deposition (MOCVD),[4,5] to our knowledge, only *n*-type doping of GaInP has been reported by chemical beam epitaxy (CBE).[6] We have investigated the *p*-type doping of GaInP by CBE using gaseous diethylzinc (DEZn) and successfully grown 0.98 $\mu$m lasers using $Ga_{0.51}In_{0.49}P$ cladding layers with all gaseous doping.

It is desirable to effect the *p*-type doping using gaseous sources rather than conventional solid sources. This ensures uniform dopant distribution across the wafer as well as long-term stability and reproducibility of doping. It also offers the possibility of abrupt doping profile changes. We have used DEZn with $H_2$ carrier gas (27% concentration) for our doping studies. This precursor has been used successfully for *p*-type doping of InP by CBE[7] and of GaAs by MOCVD[8] and CBE.[9] The GaInP epilayers were grown using triethylgallium (TEGa), trimethylindium (TMIn), and $PH_3$ on GaAs(100) oriented substrates. Lattice-matching of GaInP to GaAs within 0.1% was ensured double-crystal x-ray diffraction. The doped layers were characterized by Hall measurements, electrochemical *C-V*, and secondary ion-mass spectroscopy (SIMS) analysis.

The Zn-doped GaInP epilayers ($\sim1.0$ $\mu$m thick) for Hall measurement were grown on semi-insulating GaAs(100) oriented substrates after the growth of a 0.1 $\mu$m undoped GaAs buffer layer and a 0.1 $\mu$m thick undoped GaInP layer to avoid parasitic 2D hole gas conduction from the GaAs buffer layer. The substrate temperature was varied from 480 to 520 °C with the TEGa$+H_2$ (10%), DEZn$+H_2$ (27%), and $PH_3$ flows kept fixed at 12, 3, and 10 sccm, respectively, and the TMIn$+H_2$ (5.5%) concentration) flow varied to ensure lattice matching. The growth rate of GaInP was nominally fixed at approximately 6.5 Å/s. More details of GaInP growth have been reported elsewhere.[10] The carrier concentrations obtained from Hall measurements are shown in Fig. 1. We find that in order to obtain high *p*-type doping the substrate temperature has to be kept below about 500 °C. The Hall mobilities obtained varied from 40 to 20 $cm^2/V$ s for doping densities from $2\times10^{16}/cm^3$ to $5\times10^{18}/cm^3$. These values are in the same range as those reported for MOCVD grown *p*-type GaInP.[4] The temperature dependance of the *p*-type doping can be described by an Arrhenius-type expression $p\alpha \exp(E_A/kT)$, where $E_A$ is an apparent activation energy. The growth rate of $Ga_{0.51}In_{0.49}P$ decreases by about 8% as the substrate temperature is lowered from 520 to 480 °C. A reduced growth rate leads to increased dopant incorporation, however, this effect is not strong enough to

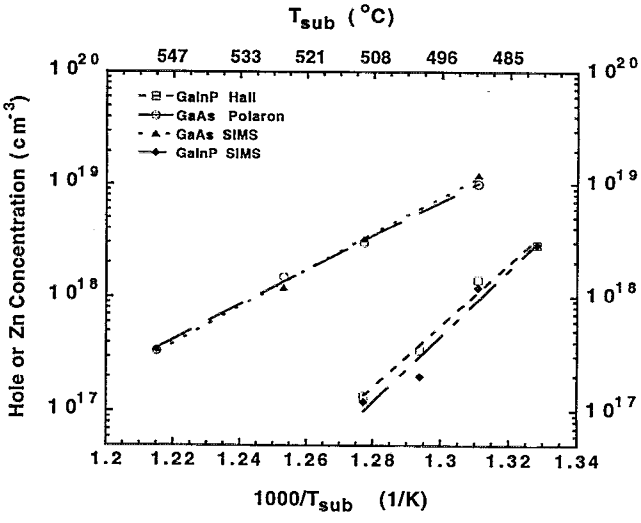

FIG. 1. Hole and Zn concentration dependance on substrate temperature for $Ga_{0.51}In_{0.49}P$. The TEGa, DEZn, and $PH_3$ flows were kept fixed while the TMIn flow was varied to ensure lattice matching to a GaAs substrate.

explain the observed exponential increase in doping concentration. The increased dopant incorporation is due to decreased desorption of the adsorbed Zn and its alkyl species from the growing crystal surface as $T_{\text{sub}}$ is reduced. The Arrhenius plot in Fig. 1 gives an activation energy of 5.35 eV for Zn doping of GaInP using DEZn. For comparison, a plot of our results for the temperature dependance of Zn doping of GaAs using DEZn by CBE is also included in Fig. 1. This data was obtained using electrochemical *C-V* (Polaron) profiling technique. This shows an activation energy of 3.0 eV for GaAs. Using MOCVD, activation energies of 1.9 eV for Zn doping of GaInP in the substrate temperature range 600–720 °C using dimethylzinc (DMZn),[4] 3.3 and 4.0 eV for Zn doping of GaAs in the substrate temperature range 575–675 °C using DEZn and DMZn, respectively,[8] have been reported. Using CBE an activation energy of 2.0 eV for Zn-doped GaAs in the temperature range 520–600 °C has been reported.[9] At a particular substrate temperature the incorporation of Zn into GaInP depends on several processes occurring on the substrate surface. These include the arrival rate of the DEZn, the pyrolysis rates of DEZn into monoethylzinc (MEZn), MEZn into Zn, the re-evaporation of all these surface adsorbed species, and the surface coverage (i.e., the availability of surface sites for adsorption). The high vacuum environment of CBE allows for only one single-bounce for the various adsorbed species and may be responsible for the higher activation energies observed compared to MOCVD which is carried out in the 76–760 Torr range.

The zinc incorporation in GaInP films was also investigated using SIMS. In the absence of a calibration standard for Zn-doped GaInP, the hole concentration of $2.85 \times 10^{18}/\text{cm}^3$ obtained from Hall measurement on one of the GaInP films was treated as a standard to quantify SIMS data. Since the electrical activity (ratio of hole concentration to Zn concentration) for Zn in GaInP is reported to be about 0.7 in the $10^{18}/\text{cm}^3$ range[5] this will lead to an underestimation of the Zn concentration. The SIMS-determined Zn concentration in the GaInP films falls on a straight line in the Arrhenius plot shown in Fig. 1. The activation energy obtained from the SIMS data is 5.7 eV, which is in good agreement with 5.35 eV obtained from the Hall data. The quantitative Zn concentration in GaAs films was determined using an ion-implanted calibration standard. The values for Zn doping of GaAs obtained by SIMS agree very well with the electrochemical *C-V* determined hole concentrations indicating absence of dopant compensation and an electrical activity of unity. The activation energy for Zn incorporation in GaAs obtained by SIMS was 3.2 eV, again in good agreement with 3.0 V obtained from the electrochemical *C-V* data. The Zn concentration profiles in GaInP obtained by SIMS are shown in Fig. 2. These data show a very stable concentration of Zn versus depth in the films which is indicative of the stability of the CBE process.

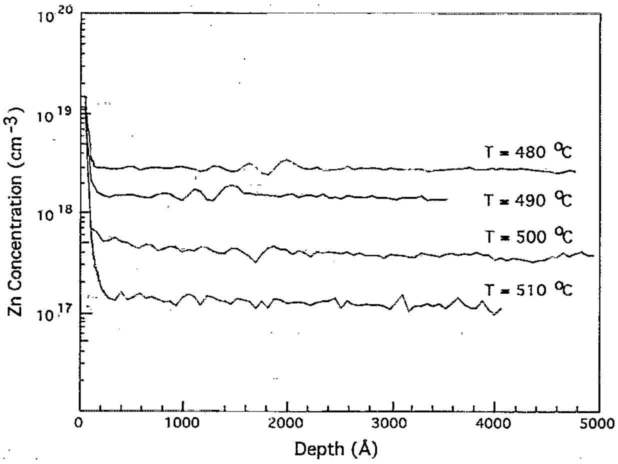

FIG. 2. Zinc concentration profiles in $Ga_{0.5}In_{0.49}P$ grown at various substrate temperatures, obtained by SIMS.

The DEZn flow dependence of zinc incorporation in GaInP films measured by SIMS is shown in Fig. 3. The group III and V flows, and substrate temperature were kept constant during the growth. At both 490 and 520 °C the zinc incorporation increases as the 0.8th power of the DEZn flow. This is the same as 0.81th power law found for DMZn mole fraction dependance for MOCVD grown *p*-GaInP.[4] A saturation in the Zn incorporation at a level of $\sim 5 \times 10^{18}/\text{cm}^3$ is observed at $T_{\text{sub}} = 490\,^\circ\text{C}$. At low DEZn flows, Zn incorporation is limited by the DEZn arrival rate since plenty of surface sites are available for adsorption. At high DEZn flows the surface sites are saturated leading to saturation in Zn incorporation. Such a saturation of Zn incorporation in InP has been reported previously.[11]

The Zn doping studies of GaInP were successfully used to grow *p*-type material for use in 0.98 $\mu$m lasers. The typical *L-I* and *I-V* curves for $500 \times 4\ \mu\text{m}^2$ ridge waveguide lasers with $I_{\text{th}} = 8$ mA are shown in Fig. 4. This laser structure uses an $In_{0.2}Ga_{0.8}As$/GaAs single quantum well structure, GaAs waveguide layers, and $Ga_{0.51}In_{0.49}P$ cladding layers. The *p*-GaInP cladding layer is Zn doped to $5 \times 10^{17}/\text{cm}^3$ hole concentration using DEZn and the *n*-GaInP cladding layer is S doped to $1 \times 10^{18}/\text{cm}^3$ electron concentration using $H_2S$. A broad-area threshold current density of 70 A/cm$^2$ has been obtained with this structure,

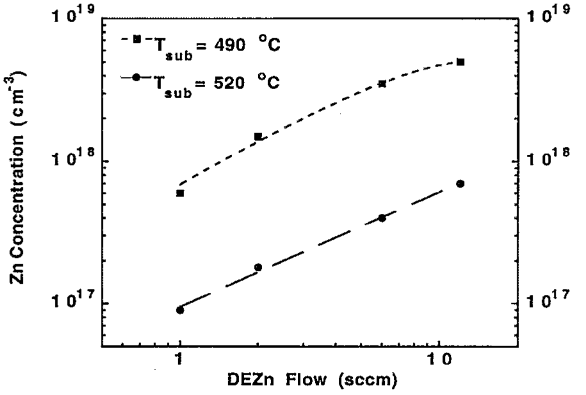

FIG. 3. The DEZn flow dependence of zinc incorporation in $Ga_{0.51}In_{0.49}P$ films measured by SIMS. The substrate temperature and growth rate were kept fixed.

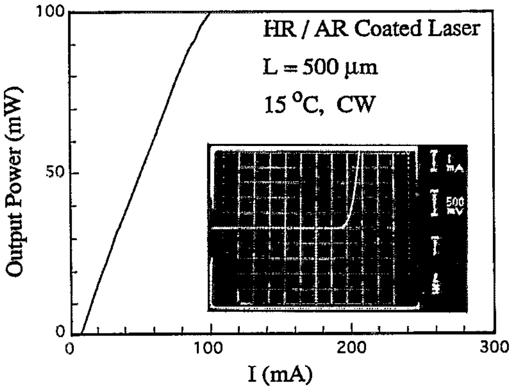

FIG. 4. The typical light-current characteristics and *I-V* characteristics of 0.98 $\mu$m strained $In_{0.2}Ga_{0.8}As/GaAs$ single quantum well lasers containing Zn-doped $p$-$Ga_{0.51}In_{0.49}P$ and S-doped $Ga_{0.51}In_{0.49}P$ cladding layers. This is a ridge waveguide structure with $500\times5$ $\mu m^2$ dimensions.

which is comparable to the best reported value of 65 $A/cm^2$ by MOVPE.[12,13] More details on laser performance have been reported elsewhere.[14]

In conclusion, we have used DEZn to obtain $p$-type doping in GaInP using CBE. The substrate temperature and the dopant flow rate dependence was studied using Hall and SIMS analysis. The doping studies led to the successful growth, by all-gaseous source CBE, of low threshold strained InGaAs/GaAs lasers using GaInP cladding layers.

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