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p-type doping of InP and $Ga_{0.47}In_{0.53}As$ using diethylzinc during metalorganic molecular beam epitaxy

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Diethylzinc (DEZn) was used as a p-type dopant source during metalorganic molecular beam epitaxy of $Ga_{0.47}In_{0.53}As$ and InP. The incorporation efficiency of the Zn was less than 10^{-3}. However, doping levels from $p = 1\times10^{17}$ to 3×10^{19} cm^{-3} were obtained at growth temperatures of 485–510 °C. Measurements with secondary-ion mass spectrometry indicated negligible diffusion of Zn in the $Ga_{0.47}In_{0.53}As$ at these doping levels and growth temperatures. The DEZn was used to dope the p-type InP cladding layer of broad-area separate confinement multiquantum well (SCH-MQW) lasers. Threshold current densities as low as 600 A/cm^2 were achieved in nonoptimized structures.

The use of the metalorganic molecular beam epitaxy (MOMBE) for the growth of $InP/Ga_{0.47}In_{0.53}As$ heterostructures is well established. High quality single layers with mobilities and photoluminescence comparable that of the best material grown by other epitaxy methods have been reported by several authors,[1–3] and excellent results have been obtained for the growth of optoelectronic devices.[4,5] However, all of this work is restricted to the use of elemental Be as a dopant source. Since there are problems arising from the reaction of hot elemental Be with decomposing metalorganics to form Be_2C in the effusion cell,[6] and occasional difficulties in obtaining low doping levels with Be,[7] we have investigated the feasibility of using Zn as a dopant in spite of its high vapor pressure.

Recently the use of volatile compounds as dopant sources in MOMBE of InP has been investigated by several authors.[8,9] For n-type doping of InP and GaAs, Weyers *et al.* report extremely low incorporation efficiencies for disilane ($< 10^{-6}$) and for tetraethyltin (10^{-4}). For p-type doping of InP they report very limited success using DEZn, diethylberyllium, and biscyclopentadienylmagnesium. However, they were able to dope GaAs with Zn using diethylzinc, DEZn, at substrate temperatures from 520 to 600 °C. The doping efficiency improved as the temperature was lowered. In light of these results, and because we often grow $Ga_{0.47}In_{0.53}As$/InP heterostructures below 520 °C, we have investigated the use of DEZn, to dope $Ga_{0.47}In_{0.53}As$ and InP. In addition, advantage could be taken of some of the potential benefits of using MOMBE: Better control of the dopant flux and the reduction of the number of hot sources in the ultrahigh vacuum (UHV) chamber during growth.

The $Ga_{0.47}In_{0.53}As$/InP heterostructures were grown in a VG-V80H MBE system which has been configured for MOMBE by the use of a 2200 ℓ/s turbomolecular pump and by modification of the sample manipulator to permit a thermocouple to be brought into intimate contact with the Mo sample holder. The group-III metalorganics [trimethylindium (TMI) and triethylgallim (TEG)] were introduced together into the system through a warm stainless-steel tube through the center port of the MBE growth chamber, that is conventionally used for an optical pyrometer. Beams of the group-V dimers, As_2 and P_2, were obtained by thermally cracking 100% AsH_3 and PH_3 in a low-pressure gas source[10] at 975 °C. The DEZn was introduced through a separate tube into one of the effusion cell ports to eliminate the possibility of cross contamination of the group-III metalorganics. The flow control method was the same for all the gasses, a fixed conductance or leak backed up by a small volume of gas which was pressure controlled to $\pm0.5\%$ of the total pressure. The metalorganics were delivered to the system without the use of a carrier gas by means of their own vapor pressure.

The layers for this study were grown on both semi-insulating and n-type (100) oriented wafers. The substrates were first cleaned with distilled chloroform, acetone, and methanol and given a final etch in 3:1:1 H_2SO_4:H_2O_2:H_2O before loading into the system. Samples were soldered to Mo sample blocks with In. The native oxide was desorbed at 510 °C with sufficient P_2 flux to prevent decomposition of the InP surface. The growth rates for InP and InGaAs were 0.8 and 1.6 μm/h, respectively. Samples were grown at 485 and 510 °C.

The samples for Hall measurements consisted of layers 400 nm thick, grown onto the semi-insulating substrates. The Hall measurements were made on samples 4 mm square using the Van der Pauw method. For $Ga_{0.47}In_{0.53}As$ $N_A - N_D$ is plotted against the pressure of DEZn, [DEZn], upstream of the fixed conductance Fig. 1. The hole concentration is proportional to $[DEZn]^2$, as expected for flow through a fixed conductance. The actual flow rates were in the range of 0.05– 5 sccm. For comparison the group-III flows are about 1 sccm for 1 μm/h growth. This means that the incorporation efficiency of DEZn is extremely low, about 5×10^{-4} at 510 °C. The incorporation at 485 °C, as we can see from the plot, is higher by a factor of 3. These data suggest that the DEZn is completely decomposed over the entire growth temperature range since neither the pressure dependence or the temperature dependence of the carrier concentration that were observed are consistent with

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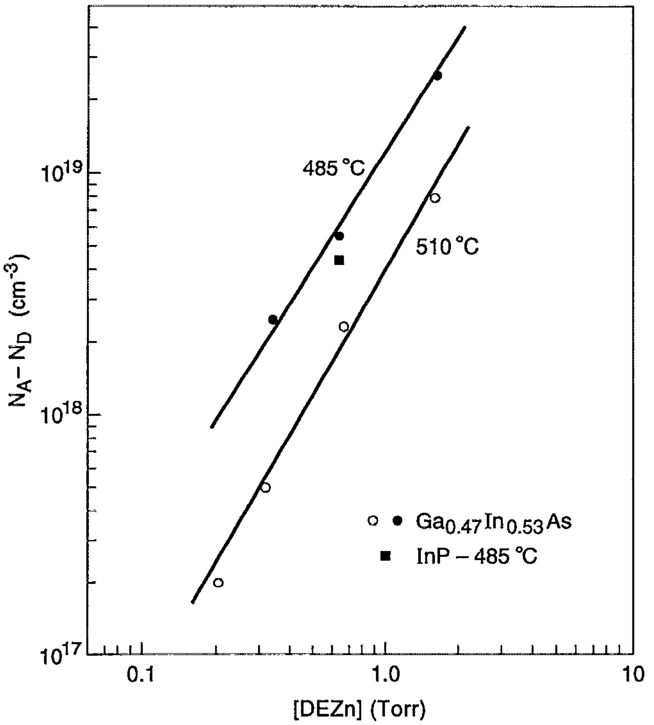

FIG. 1. Net hole concentration vs DEZn pressure measured upstream of the fixed conductance in the gas handling system. Sample growth temperatures are 510 and 485 °C.

partial decomposition. The latter would be strongly temperature dependent, opposite to the dependence observed, and probably also pressure dependent.

The highest hole concentration reached in $Ga_{0.47}In_{0.53}As$ was 2.6×10^{19} cm^{-3} at a substrate temperature of 485 °C. The lowest was 1.5×10^{17} cm^{-3} at 510 °C. The latter was lower than we had been able to achieve previously with Be, which is believed to react with oxygen[7] making it difficult to dope at low levels unless the system is very free of oxygen containing vapor species. For the doping of InP one preliminary Hall measurement suggests similar behavior to that observed with $Ga_{0.47}In_{0.53}As$. The Hall mobilities shown in Fig. 2 exhibit no unusual features. However, extrapolation of these data to higher doping levels yields lower mobilities than we have previously observed for extremely high Be doping in $Ga_{0.47}In_{0.53}As$.[11]

A heterostructure that was grown for secondary-ion mass spectrometry (SIMS) measurements is illustrated along with the SIMS results in Fig. 3. It contained 5 $Ga_{0.47}In_{0.53}As$ layers, each 150 nm thick, separated by InP layers 50 nm thick. The DEZn beam impinged on the growing surface during growth of the center 50 nm of each ternary layer. The first two regions were grown at 510 °C with Zn concentration, based on the Hall measurements, intended to be 2.5×10^{18} and 9×10^{18} Zn/cm^3. The last three regions were grown at 485 °C with intended concentrations of 4.5×10^{18}, 1×10^{19}, and 2.5×10^{19} Zn/cm^3. The concentrations measured by SIMS are lower than intended by a factor of about 1.5–2.5. This difference is probably within the experimental error of the Hall and SIMS mea-

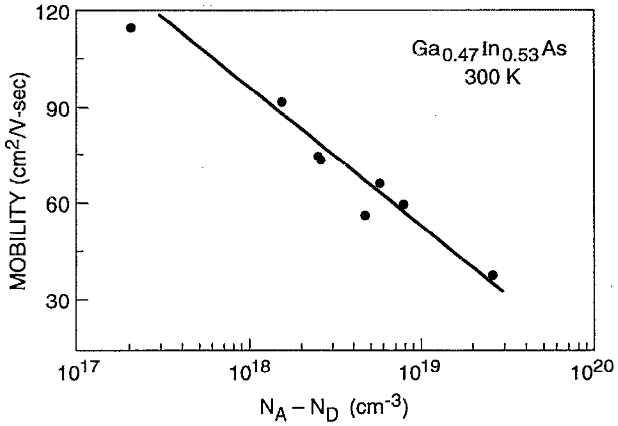

FIG. 2. Hall mobility against net hole concentration for Zn-doped $Ga_{0.47}In_{0.53}As$ at 300 K.

surements. The most important feature is the sharp profile of the Zn spectra for all doping levels, showing no measurable redistribution from diffusion or surface segregation. The leading and trailing edges of the Zn profiles have almost the same slope as that of the As profile, indicating very sharp interfaces for Zn, since we know that the heterostructure interfaces are almost atomically abrupt.[12]

Outside of the deliberately doped regions in the sample illustrated in Fig. 3, there is a significant background level of Zn. Furthermore, when layers that are not deliberately doped are grown subsequent to the use of DEZn, they are found to be electrically compensated. This indicates a "memory" effect due to a buildup of DEZn or elemental Zn on surfaces of intermediate temperature in the system. It is eliminated by heating the sample holder and group-V cracker, while allowing the LN_2-cooled cryopanels to warm up. The small Zn peaks observed in the InP layers shown in Fig. 3 are most likely due to Zn accumulation at the interface during the 30 s growth interruption between layers because of the high background levels.

To evaluate the electrical characteristics of the incor-

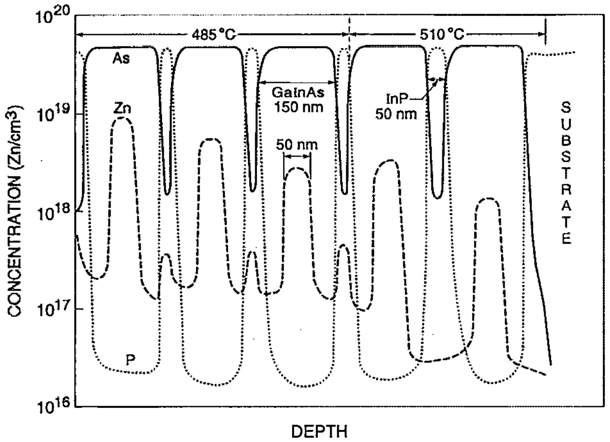

FIG. 3. SIMS profile of Zn pulses in $Ga_{0.47}In_{0.53}As$ for several different doping levels and growth temperatures. The widths of the InP- and Zn-doped GaInAs regions appear to be different because InP etches more rapidly than GaInAs during the SIMS analysis.

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porated Zn for use in devices, simple *p-n* homojunctions and broad-area separate confinement heterostructure multiquantum well (SCH-MQW) laser structures were grown. The *p-n* homojunctions were heavily *p* doped, and more lightly *n* doped, to about $p = 10^{19}$ cm^{-3} and $n = 10^{16}$ cm^{-3}, as might be useful for bipolar transistors. They had low breakdowns (1–2 V) and large reverse leakage currents. This may be due to either to contamination of the *n*-doped layer by the background Zn or may result from the low doping efficiency and thus large DEZn flux needed for the high doping. It is possible that the very large coverages of the surface with DEZn, that are required for high doping, may interfere with the epitaxy and result in growth-related defects.

For the laser structure the *p* doping was 7×10^{17} cm^{-3} in the InP cladding layer illustrated in the inset in Fig. 4. The lasers were electrically pumped and had thresholds in the 700 A/cm^2 range with the lowest value at 600 A/cm^2 (Fig. 4). The structure illustrated was not optimized for low threshold, nevertheless the thresholds obtained are respectable. This first reported use of Zn as a dopant in a reasonably good device grown by MOMBE without optimization suggests that there may be a role for Zn doping, at least in the lower doping range, for MOMBE-grown $Ga_{0.47}In_{0.53}As/InP$ heterostructures.

In summary, we have shown that Zn derived from DEZn is potentially useful as a *p*-type dopant in MOMBE. Doping levels up to $p = 2.5\times10^{19}$ cm^{-3} have been measured in $Ga_{0.47}In_{0.53}As$. The SIMS data show no apparent diffusion at these levels. However, because of the very low incorporation efficiency, $<10^{-3}$, very high DEZn fluxes are needed to achieve high doping. These high fluxes cause memory effects as the result of system contamination, and may interfere with the growth giving poor epitaxy. At low flows we were able to use DEZn to grow near- state-of-the-art broad-area SCH-MQW lasers, demonstrating that in some applications Zn may be a suitable *p*-type dopant for MOMBE, even at this early stage of investigation.

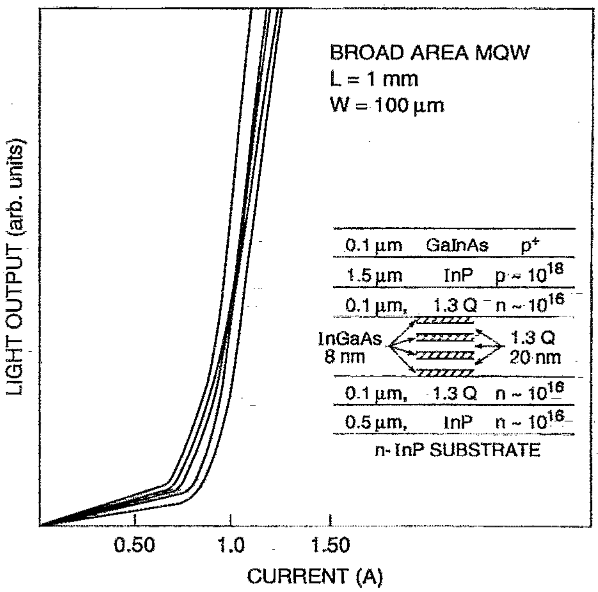

FIG. 4. Light-current characteristics for several randomly selected broad area SCH-MQW lasers. The inset shows the laser cross section. The notation 1.3Q indicates the GaInAsP quaternary with a band-gap wavelength of 1.3 μm.

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