Low-temperature rapid thermal low pressure metalorganic chemical vapor deposition of Zn-doped InP layers using tertiarybutylphosphine

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High purity Zn doped InP layers were grown by rapid thermal low pressure metalorganic chemical vapor deposition technique, using tertiarybutylphosphine as the phosphorus source. The best quality layer, which was grown at P:In ratio of 75, temperature as low as 525 °C, pressure of 2 Torr and growth rate of 2 nm/s, exhibited electron mobility of 80 $cm^2 V^{-1} s^{-1}$ and Hall carrier concentration of 3.5×10^{18} cm^{-3} at room temperature. The stoichiometry of the InP Zn-doped layer was excellent, regardless of the Zn content in the reactive gas mixture. The crystallographic defect density and the surface morphological particle concentration, however, were found to be strongly dependent on the Zn concentration.

The growth of III-V semiconductor films by means of rapid thermal low pressure metalorganic chemical vapor deposition (RT-LPMOCVD) technique had been demonstrated successfully for the growth of GaAs and AlGaAs on GaAs substrates,[1,2] and recently for the growth of undoped InP films on InP substrates.[3] This technique uses rapid and precise changes in the substrate temperature, driven by switching on and off halogen-tungsten lamps, in order to control layer growth, rather than applying gas flow switching concepts, normally used in the standard metalorganic chemical vapor deposition (MOCVD) technique. Thus, multilayer heterostructures, multiquantum well structures, and any generic semiconductor structure that comprises a well-defined semiconductor/semiconductor interface, may benefit from the execution of the RT-LPMOCVD technique. This is due to the fact that the RT-LPMOCVD technique carries the potential of a better control of the semiconductor monolayer growth as a result of the rapid elevation and reduction of the wafer temperature. In particular, controlled incorporation of dopants, such as Zn, into semiconductor grown layers, is essential for the formation of well-defined structures, such as *p-n* junctions in InP-based photonic and electronic devices.[4,5] In addition it enhances the creation of highly doped p^+ regions to support high performance ohmic contact on these type of devices.[6,7]

In this letter, we present results that reflect the quality of Zn-doped InP epitaxial layers, which were grown by means of the RT-LPMOCVD technique, onto an InP substrate.

InP layers were grown on Fe-doped, semi-insulating InP substrates with (100) orientation, by the RT-LPMOCVD technique, using an A. G. Associates Heatpulse CVD-800™ system. This is a low pressure, load locked, horizontal, and laminar flow reactor, heated by two sets of high power halogen-tungsten lamps (12 lamps of 1.5 kW each) and is capable of processing a single wafer under inert, hazardous, or corrosive ambients.[8] The quartz chamber is 10 in. long with an elliptic cross sectional shape, 4 in. wide and 1 in. high. Prior to the growth, the InP substrates were cleaned by flushing sequentially with chloroform, acetone, and methanol, followed by a sequence dipping in H_2SO_4, H_2O_2, and deionized water, and finally blown dry with filtered N_2, and immediately loaded into the reactor. Trimethylindium (TMIn) (at 50 °C), tertiarybutylphosphine (TBP) (at 0 °C) and diethylzine (DEZn) (at 0 °C) were used as the indium, phosphorus, and zinc sources, respectively. Hydrogen, purified by a palladium diffuser, was used as the carrier gas for the indium metal organic precursor.

The optimum growth conditions were evaluated by modifying the key growth parameters, such as temperatures, at the range of 450–550 °C pressures, at the range of 1–5 Torr, and growth durations at the range of 30 s–10 min resulting in growth rates of up to 130 nm/min. For these conditions the following optimum flow rates were defined: 75 standard cubic centimeter per minute (sccm) of TBP, 1 sccm of TMIn, and 1 sccm of DEZn. For the latter, a main flow controller with a total range of 10 sccm was used in order to provide a better accuracy.

Rutherford back scattering (RBS), transmission electron microscopy (TEM), double crystal x-ray diffractometry, and secondary ion mass spectrometry (SIMS), were used to characterize the Zn-doped InP film quality and properties. Room-temperature Hall measurements (Hg-In alloyed contacts) were used to obtain the sample sheet resistance and mobility. The RBS was performed on a 1.8 MeV Van der Graf generator, using a He^+ ion beam. The SIMS measurements were performed on a Cameca IMS-4*f* system, using a Cs^+ ion beam. The impurity concentrations were derived from a comparison of their results with spectra taken from ion-implanted InP standards.

Figure 1 shows a typical RT-LPMOCVD processing chart, as was applied in order to grow the Zn-doped InP layers. Initially the wafers were loaded, the chamber was pumped down to background vacuum of 1×10^{-7} Torr, and then an *in situ* surface cleaning of the wafer was realized by means of heat pulsing the wafer to a temperature of 580 °C for 120 s under TBP flow at pressure of 2 Torr. The TBP was used in order to provide the H_2 for the wafer

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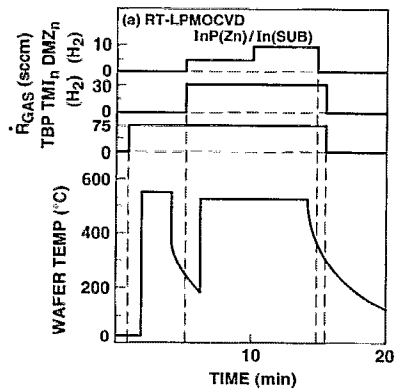
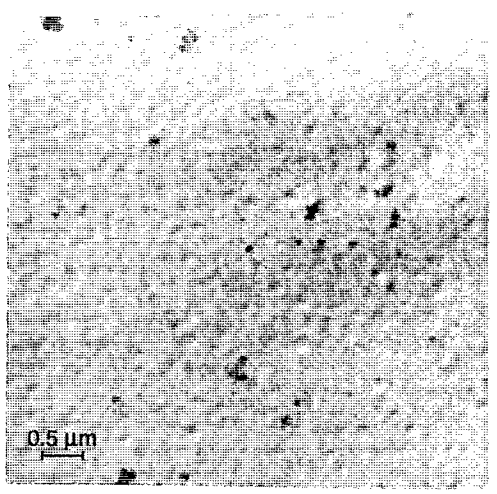


FIG. 1. Schematic process flow chart of a RT-LPMOCVD Zn-doped InP layer (100 thick).

cleaning and p^+ to protect the wafer surface. Subsequently, the wafer was cooled down to temperatures below 200 °C, TMIn, and DMZn mass flow controllers were opened to form and stabilize the reactive gases environment in the chamber, and then the lamps were turned on to heat the substrate to the reaction temperature and initiate the deposition. The process was completed after 1–10 min by turning the lamps off and subsequently terminating the gas flow into the chamber.



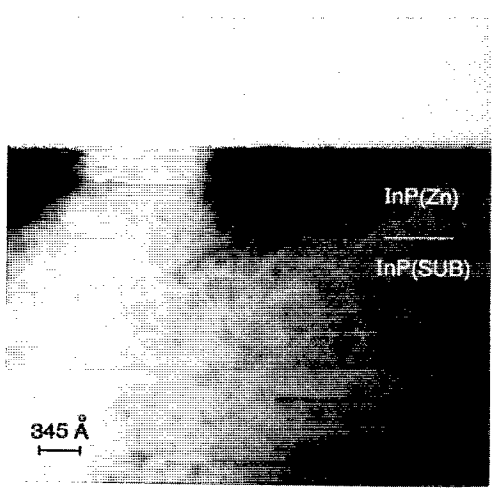


FIG. 2. Bright-field TEM micrographs of Zn-doped RT-LPMOCVD InP layer grown on SI-InP substrate at 475 °C for 5 min.

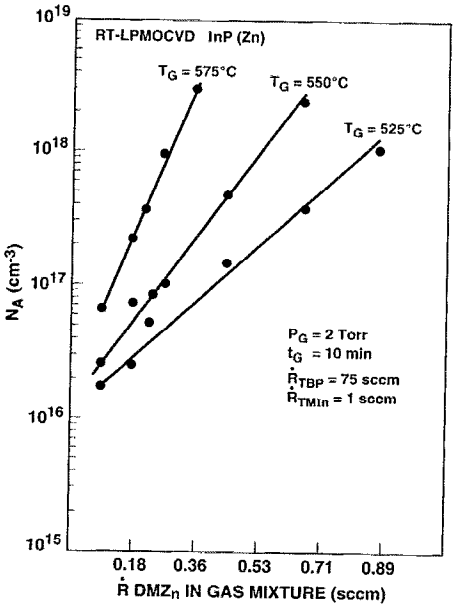


FIG. 3. Carrier concentration (N_A) at Zn-doped RT-LPMOCVD InP layer, as a function of the DMZn flow rate and the growth temperature.

The quality of the Zn-doped InP layers was examined by double crystal x-ray diffractometry, which yielded a well-defined and narrow single peak with a 22 arcsec full width at half-maximum (FWHM) of the InP peak. The film crystallinity was checked by the RBS analysis which revealed a minimum in peak yield (λ_{min}) of 3.4% of a crystal defect-free film, suggesting an excellent epitaxial growth.

The quality of both the RT-LPMOCVD Zn-doped InP film and the $InP_{(eip)}/In_{(sub)}$ interface was inspected by means of TEM studies as well. The TEM plan view and cross section of a 50 nm layer are given in Fig. 2, revealing a very high quality, featureless grown films with sharp interface to the substrate.

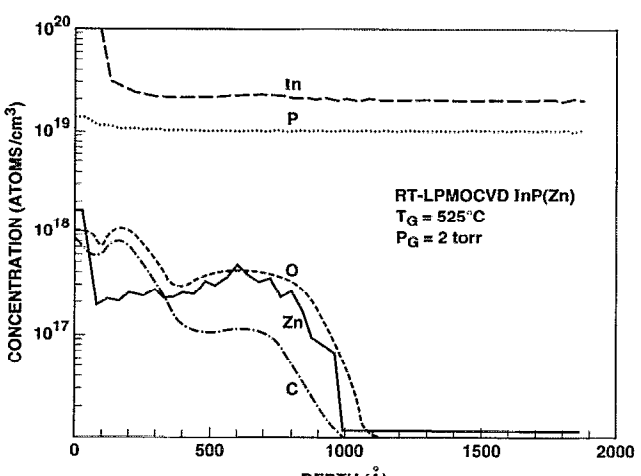


FIG. 4. SIMS depth profile of Zn-doped RT-LPMOCVD InP layer grown on SI-InP substrate at 525 °C for 2 min.

The featureless layers were measured to have a *p*-type background doping levels of $Na \geqslant 5\times10^{16}$ cm^{-3}, with a concentration higher than 5×10^{17} cm^{-3}, while grown at a preferred set of reactive gas mixture and in particular with high DMZn flow rate, and temperature conditions, as is demonstrated at Fig. 3.

The concentration of the oxygen and carbon impurities, in addition to the zinc, in the RT-LPMOCVD InP films were analyzed by SIMS, and found to be about 4×10^{17} and 1×10^{17} cm^{-3}, respectively, as is shown in Fig. 4. These films, which were grown at temperature of 525 °C and pressure of 2 Torr, had a Zn doping level of 2.5×10^{17} cm^{-3} or higher (see Fig. 4), and a 300 K mobility of about 80 cm^2 V^{-1} s^{-1}.

The deposition kinetics of the RT-LPMOCVD Zn-doped InP layers, were evaluated by combining both RBS and TEM direct film thickness measurements. These data are given at Fig. 5, suggesting that by increasing the process chamber pressure to 3 Torr and the deposition temperature to 550 °C, a maximum growth rate of about 130 nm/min was achieved. It was also defined that a minimum temperature of 475 °C is required in order to realize the deposition of Zn-doped InP layers. While applying this minimum temperature at deposition pressure of 3 Torr, a growth rate of about 70 nm/min was achieved. These rates are comparable to the InP growth rates that were obtained by means of conventional MOCVD. In this case a growth rates at the range of 15–150 nm/min were achieved while applying temperatures in the range of 550–650 °C, respectively, with a group V to group III gas flow rate ration of 50.[9–11]

In summary, we have demonstrated the RT-LPMOCVD growth of a good quality epitaxial Zn-doped InP layers into InP substrates. These layers were extensively analyzed, and have exhibited as good properties as the similar conventional MOCVD Zn-doped InP layers. It is, however, important to note that the RT-LPMOCVD technique allowed the growth of good quality Zn-doped InP layers already at temperatures as low as of 475 °C.

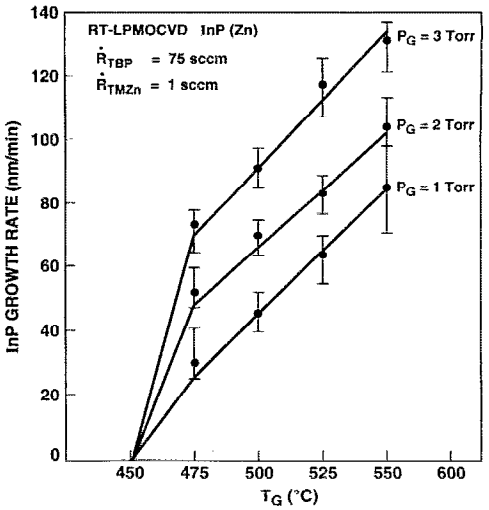


FIG. 5. RT-LPMOCVD Zn-doped InP layer growth rate as a function of the growth temperature and the chamber pressure.

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