Low-pressure MOVPE: the time of the pioneers

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In 2020, the technology "Low-pressure Metal Organic Vapor Phase Epitaxy" is so universally widespread that it seems essential. Almost everybody on earth owns or has seen LED indicators or displays, LED lightings, remote controls, mobile phones, barcode products, and more than half have access to the internet… In all these devices and services, there are components made of III-V semiconductors whose manufacturing requires one or several "Low-pressure MOVPE" epitaxy steps. Out of habit, we have removed the prefix to keep only the name MOVPE. The precursors of the MOVPE technique (Harold Manasevit, Russ Dupuis, Gerald Stringfellow, Takatosi Nakanisi, S.J. Bass, Jean-Phillipe Hallais, and many others) used reactors operating at atmospheric pressure at the beginning of the epic. It took a lot of time and effort to convince the scientists and engineers of the late 1970s of the merits of reduced pressure.

And yet, operating an III-V heterostructure growth reactor under reduced pressure has undeniable advantages for the mass production of components intended for telecoms or lightings : First it reduces the parasitic reactions caused by homogeneous nucleation in the gas phase because of the reactants partial pressures which are lower, secondly it reduces the flowing gas heating. These two characteristics allow the construction of very large reactors ; and furthermore, it is possible to find growth conditions: hydrogen flow, pressure, growth rate such that gas are renewed in the reactor in a time less than the growth of an atomic plane of material, which allows complex heterostructures to be produced with the same precision as the molecular beam epitaxy, but at a reduced cost.

A III-V compounds low pressure OMVPE reactor required that the gas control panel be maintained at atmospheric pressure to allow easy switching vent to reactor, a needle valve ensured the "jump" of pressure between this panel and the reactor, a rough pump maintained a working pressure at the wanted value (generally of one tenth of an atmosphere) regardless of the hydrogen flow, the working pressure in the reactor was controlled by limiting the pumping rate by means of an almost closed control valve whose clogging was avoided by gas 3 D filtering provided by a glass wool pad. Finally, a low-grade nitrogen flow was added at the outlet of this pump prevented the re-entry of oxygen at the time of its return to atmospheric pressure.

At the time of the pioneers, the purity of the starting products was weak : the organometallic contained diethyl ether (solvent for their synthesis containing oxygen), the arsine contained moisture and the phosphine was contaminated with traces of arsine ; it was necessary to " juggle" with the growing conditions to minimize the influence of these impurities on the grown layer quality : the oxygen was fixed on the Aluminum of the GaAlAs layers and created a deep level which made them insulating. By favoring parasitic deposits on the reactor walls upstream of the deposition zone, the oxygen, was partially trapped, creating a "gettering effect" which purified the gaseous phase in situ and limited the oxygen incorporation. This is how our first GaAs / GaAlAs laser diodes were grown in 1978. Later, a reactor was specially built and dedicated to the study of the oxygen incorporation kinetics in GaAlAS, its mechanism understanding made it possible to better reduce the GaAlAs films oxygen contamination. Phosphine contained some traces of arsine, but since arsenic is more easily incorporated into the GaInAsP layers than phosphorus, it was difficult to grow high quality InP. The "trick" consisted of introducing the phosphine through a pyrolysis oven which cracked arsine without significantly affecting phosphine, then the arsenic vapor condensed out of the oven and did not participate in growth. In the period 1973-1978 three low-pressure reactors were built : A first one for silicon in 1973 (94 GHz IMPATT diodes, PIN, varactors) ; a second one for GaAs / GaAlAs in 1975 (Schottky diodes, varactors, 850 nm laser diodes, image intensifier, FETs); a third one for InP and its alloys in 1977 (94 GHz Gunn diodes, voluntary mismatch GaInAs for forecasting crops from space in the Spot 4 satellite).

In the period 1980 to 1985, our group demonstrated the feasibility of many components operating around 1300 nm and 1500 nm for fiberoptic telecommunications, it produced low current density threshold GaAlAs/GaAs SCH and GRINSCH laser diodes , it showed 2 D electrons or holes gas layers at the interface of several III-V heterostructures, then it provided epilayers for several space programs and for the innovative 850 nm multimode fiberoptic Biarritz project.