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# III–V semiconductor devices grown by metalorganic chemical vapor deposition—The development of the Swiss Army Knife for semiconductor epitaxial growth

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## ABSTRACT

Metalorganic chemical vapor deposition (MOCVD) epitaxial materials technology for the growth of compound semiconductors has been developed over the past 60-plus years to become the dominant process for both research and production of light-emitting devices as well as many other electronic and optoelectronic devices. Today, MOCVD has become the “Swiss Army Knife” of semiconductor epitaxial growth, covering a wide variety of compound semiconductors and device applications. Because of the flexibility and control offered by this process and the material quality produced by MOCVD, many important III–V semiconductor devices have become commercially viable. This paper attempts to provide a personal view of the early development of MOCVD and some brief historical discussion of this important and highly versatile materials technology for the growth of high-quality devices employing ultrathin layers and heterojunctions of III–V compound semiconductors, e.g., quantum-well lasers, light-emitting diodes, heterojunction solar cells, transistors, and photonic integrated circuits.

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## I. INTRODUCTION—THE DEVELOPMENT OF EPITAXIAL GROWTH

The term “epitaxy” is derived from the Greek word roots “*epi*”—“above” and “*taxis*”—“in an ordered manner” and refers to the deposition of an ordered atomic arrangement of one type of crystalline material (the “film” or “epitaxial layer”) upon another crystalline surface (the “substrate”) with a specific registration of the lattice atoms of the two crystals. Epitaxial growth processes have occurred naturally for eons on Earth.<sup>1</sup> A common example of “naturally occurring epitaxy” is the growth of rutile, TiO<sub>2</sub>, on hematite, Fe<sub>2</sub>O<sub>3</sub>. The term “epitaxy” (“l’épitaxie”) may have first been used in 1928 by M. Louis Royer in France to describe the structural characteristics of the growth of various crystalline salts, e.g., AuCl, on other crystalline salts, e.g., rock salt, NaCl.<sup>2,3</sup>

The invention of the Ge bipolar transistor (a point-contact semiconductor device) on December 16, 1947 by John Bardeen and Walter H. Brattain at the Bell Telephone Laboratories (BTL) in Murray Hill, NJ,<sup>4</sup> greatly accelerated the study of the properties of semiconductors. Along with the increased fundamental research, the practical development of this device required better control of the materials properties of the device structures, especially for the *p-n* junction version of the transistor, developed beginning in 1948.<sup>5,6</sup> This led to studies of how to create semiconductor layers with controlled electrical properties. The epitaxial growth of thin planar crystalline layers of semiconductors was studied as early as 1950–1952 by Gordon Teal and Howard Christensen at BTL—also known as Bell Labs, who applied for a patent for a vapor-phase process for the growth of Ge epitaxial layers in 1951.<sup>7,8</sup> Earlier in 1950, Teal *et al.* had reported the growth of Ge

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*p-n* junctions having nearly ideal *I-V* characteristics fabricated from bulk Ge crystals grown with the controlled sequential introduction of *n*-type and *p*-type impurities to create a *p-n* junction.<sup>9</sup> These results encouraged Teal to work on a more controlled process of producing individually doped layers. Earlier in 1946, Teal had reported the vapor transport of Si using SiCl<sub>4</sub> in a CVD process, but this was for deposition of polycrystalline films.<sup>10</sup> The 1951 Christensen and Teal patent<sup>7</sup> describes an “open-tube” vapor-phase epitaxial (VPE) growth process for Ge films, and this may represent the “genesis” of all of the VPE processes used today, including MOCVD. The controlled vapor-phase epitaxial growth of semiconductor thin films was further studied in the period 1958–1961 for, e.g., Ge,<sup>11</sup> Si,<sup>12</sup> and GaAs.<sup>13</sup> The 1961 chloride-VPE growth of GaAs by R. L. Newman and N. Goldsmith at the Radio Corporation of America (RCA) Laboratory in Somerville, NJ, may be the first open-tube III–V epitaxial growth.<sup>13</sup>

Interestingly, the development of liquid-phase epitaxial (LPE) growth of semiconductors can be traced back to the year before the first VPE work. In 1950, Robert N. Hall and William C. Dunlap at the General Electric Research Laboratory in Schenectady, NY (now Niskayuna, NY) reported the development of the “alloy-junction” process for the growth of Ge *p-n* junctions.<sup>14</sup> This process is essentially “localized LPE” since upon heating, the localized melt dissolves some of the original crystal surface, and then during cooling, some of the dissolved material is redeposited back as an epitaxial crystalline material on to the surface in a small-area region, in this case, with different dopings. Thus, it can be claimed that both VPE and LPE epitaxial growth of semiconductors are over 70 years old.

## II. EARLY MOCVD EPITAXIAL GROWTH OF COMPOUND SEMICONDUCTORS

The development of MOCVD has a somewhat complicated history.<sup>15,16</sup> Interestingly, the first report of the synthesis of an organometallic compound was made by a French chemist Louis-Claude Cadet de Gassicourt (1731–1799) in 1757 when he formulated the organoarsenic compound tetramethyldiarsine, also known as cacodyl [(CH<sub>3</sub>)<sub>4</sub>As<sub>2</sub>] by accident while doing chemical research on “invisible inks” at the Hotel Royal des Invalides in Paris.<sup>17–19</sup> Further work on this class of chemical compounds was done by Robert W. Bunsen in Germany during 1837–1843.<sup>20</sup> For historical comparison with the first (CH<sub>3</sub>)<sub>4</sub>As<sub>2</sub> synthesis, the much simpler hydride arsine, AsH<sub>3</sub>, was first synthesized and identified somewhat later in 1775 by Carl Scheele in Sweden during his experiments with the reduction of arsenic(III) oxide with zinc and an acid.<sup>21</sup> Trimethylgallium was synthesized as early as 1933 by Charles A. Kraus and Frank E. Toonder at Brown University in Providence, RI.<sup>22</sup> So the MOCVD growth of GaAs could have been performed as early as 1933!

There are reports of early 1960’s studies of the reactions of column III metalorganics with column V hydrides,<sup>23</sup> and Thomas R. Scott *et al.* working at Standard Telephones and Cables (STC) in the United Kingdom<sup>24</sup> applied for a patent describing an epitaxial process involving column III metalorganics and column V hydrides in 1953.<sup>25</sup> However, it is not clear that any epitaxial growth was actually attempted. In 1961, Robert A. Ruehrwein, a chemist working at Monsanto Corporation, submitted his first patent

application for VPE growth of III–V compound semiconductors—including the use of metalorganic column III compounds as sources.<sup>26</sup> Ruehrwein’s ideas on III–V epitaxy were formed during and after a visit in late 1960 with Nick Holonyak, Jr., then working at General Electric Electronics Park in Syracuse, NY.<sup>27</sup> During 1960–1962, Holonyak developed the bulk and epitaxial growth of GaAs<sub>1-x</sub>P<sub>x</sub> III–V ternary alloy semiconductors using a closed-tube halogen-transport VPE approach and demonstrated the first III–V alloy semiconductor heterojunctions and visible light-emitting diodes (LEDs) and laser diodes.<sup>27,28</sup> The closed-tube halogen vapor-transport process for III–V “bulk growth” was developed in 1959 by George R. Antell and D. Effer at Metropolitan-Vickers Electrical Co. Ltd., Manchester, England, for the growth of small spontaneously nucleated “bulk” crystals of binary III–V compounds, e.g., InAs, InP, etc.<sup>29</sup>

Because Holonyak’s seminal work in the closed-tube epitaxial growth of direct-bandgap ternary III–V semiconductor devices was partially government-sponsored, he was obligated to share this research with other companies designated by the U.S. Government. In the 1960–1962 period, Ruehrwein and Forrest V. “Frosty” Williams, both chemists from the Monsanto Company in St. Louis, MO, visited Holonyak’s GE-Syracuse laboratory several times and observed Holonyak’s closed-tube vapor-transport apparatus, and in a late 1960 visit, Ruehrwein commented “I can do that open-tube!”<sup>30,31</sup> Subsequently, Ruehrwein wrote up and filed a patent application (originally filed on July 31, 1961) that covered on all of the VPE processes he could think of, including metalorganic sources.<sup>26,32</sup> However, there is no record of Ruehrwein or the Monsanto team of ever reducing this “MOCVD” idea to practice perhaps because they quickly and successfully developed open-tube hydride VPE for the production of GaAsP red LEDs, and the column III MO source compounds were not readily available at that time.<sup>33</sup> The 1953 patent of Scott *et al.* and the 1961 patent of Ruehrwein covering MOCVD were not reduced to practice (as far as I can tell). In the early 1960s, other researchers also patented the use of group III-A metalorganic compounds as sources for these elements. For example, in 1963, Walter Miederer *et al.* at Siemens in Germany filed a U.S. patent application for a vapor phase process using metalorganic compounds of Ga, e.g., triethylgallium and trimethylgallium, and AsCl<sub>3</sub> as sources combined with dopant sources of “alkyls of zinc, cadmium, selenium or tellurium.”<sup>34</sup> Again, it is not clear that any reduction to practice was attempted.

Dr. Harold M. Manasevit (known by his colleagues as “Hal”), then working in the Electronics Research Division of the Autonetics Group of the North American Rockwell Corp.,<sup>35</sup> began work on the development of MOCVD in 1967, 2 years after the Monsanto patent was granted. In fact, Manasevit was not aware of any of these earlier patents since there were no reports in the open literature describing the “reduction to practice” that he was aware of, so he assumed that he was the first to conceive of and actually use MOCVD. In January 1968, he published his first paper on the MOCVD heteroepitaxial growth of GaAs on sapphire (Al<sub>2</sub>O<sub>3</sub>) and other single-crystal insulating oxide substrates, e.g., spinel, beryllium oxide, and thorium oxide.<sup>36</sup> In fact, this paper did not discuss the actual process he used to grow GaAs heteroepitaxial films on single-crystal oxide substrates because his company was trying to patent this MOCVD process and they wanted to hide the details. They found out during a patent examination that Ruehrwein and

Miederer had already patented MOCVD.<sup>32</sup> In a conference talk presented in 1968<sup>37</sup> and in a later paper, Manasevit published his first complete description of his MOCVD process.<sup>38</sup> Ultimately, 17 years after the Monsanto applied for their “VPE patents,” in 1978 Rockwell again applied for their patents on MOCVD and this time they were granted in 1983!!!<sup>39,40</sup> In 1997, the Rockwell ‘098 patent was ruled invalid by a United States Federal Court.<sup>41</sup> Subsequently, it was reinstated upon appeal by Rockwell. So, 15 years AFTER Manasevit’s first paper was published in January 1968, he finally got his patents in January 1983!

Manasevit was a chemist who had received his Ph.D. from the Illinois Institute of Technology (IIT) in 1959. His Ph.D. research topic was in Physical Inorganic Chemistry working on Lewis acids—electron pair acceptors, e.g.,  $\text{Ga}(\text{CH}_3)_3$ , and Lewis bases—electron pair donors, e.g.,  $\text{AsH}_3$ , and he knew that such reactions would result in the formation of a covalent bond. In 1960, Manasevit joined the Autonetics Division of North American Aviation (NAA) in Anaheim, CA. In 1964, he developed a VPE process using  $\text{SiCl}_4$  in  $\text{H}_2$  for the growth of Si on sapphire (SOS).<sup>42</sup> His primitive SOS epitaxial reactor employed a small atmospheric-pressure “open-tube” quartz reactor chamber, a small ~2 in. diameter graphite susceptor with RF heating, and an “all-glass” gas panel composed of Pyrex tubing, grease-lubricated stop-cock valves, and a Pyrex Hg-vapor diffusion vacuum pump, backed by a standard oil-based roughing pump. The gas flow rates were controlled and monitored manually using Brooks variable-area glass flow meters called “Rotameters”—flow control valves using a small glass tube with a glass or metal spherical “float” inside combined with an O-ring-sealed needle valve for control. These crude flow meters were “individually calibrated” to an accuracy of a few percent, in principle. They are still made and sold today.<sup>43</sup>

The reason for Manasevit’s interest in the growth of semiconductors on insulating oxides (a very novel topic at that time) was that North American Aviation—which subsequently became North American Rockwell, and then Rockwell International—was the prime contractor for the guidance computers developed in the late 1950s and early 1960s for the U.S. Minuteman I ICBMs (and later for the Minuteman II and III missiles), and the NAA Autonetics Division in Anaheim, CA, was building the missile guidance systems initially using (somewhat primitive) Si devices.<sup>44,45</sup> There was, of course, concern regarding the stability of these guidance systems in a high-radiation environment since the missiles needed to be guided accurately to their targets—sometimes passing through a cloud of intense radiation. Autonetics designed the Minuteman I Model D-17B guidance computer with Si-based “diode-resistor” and “diode-transistor” logic.<sup>46,47</sup> The resistivity of the “high-resistivity” Si substrate used in these devices was destroyed by such radiation, and Manasevit knew that the electrical and physical properties of the oxide insulators would be much more stable in regard to radiation exposure. Thus, in 1963–1964, he studied, developed, and patented a VPE process for the heteroepitaxial growth of Si films on single-crystal sapphire—SOS—because Si heteroepitaxial films grown on this oxide substrate resulted in best films.<sup>42,48,49</sup> Eventually, both RCA and Hewlett–Packard developed commercial CMOS devices using SOS.<sup>50</sup> SOS is still used for “radiation-hardened” electronics, and SOS devices are still commercially

available. Furthermore, SOS electronics is the precursor to all silicon-on-insulator (SOI) devices.<sup>51</sup>

Manasevit’s work on MOCVD growth of GaAs was based on this concept of exploiting the advantages of insulating oxide substrates as applied to III–V compound semiconductors. At that time, there was an increasing interest in the development of GaAs-based high-frequency field-effect transistors and the only truly “semi-insulating” GaAs substrates with resistivities of  $> 10^8$  Ohm cm, required for this work, were at that time grown by the Czochralski process using heavy chromium doping.<sup>52</sup> The Cr doping created deep levels in the bandgap that trapped electrons, making the crystals semi-insulating. However, GaAs boules grown in this way had a wide variation in Cr concentrations and corresponding variations in electrical resistivity, and also this material tended to convert to “lightly insulating” or even conducting electrical properties under thermal annealing at typical epitaxial growth temperatures.<sup>53</sup> This property made Cr-doped GaAs an unreliable insulating substrate. Manasevit believed that he could circumvent this problem by growing GaAs layers epitaxially (as well as layers of other III–V semiconductors) on insulating oxide substrates—in analogy to his work on SOS. Manasevit accomplished this by using the Lewis acid—Lewis base ideas from his Ph.D. thesis. Manasevit’s “invention” of MOCVD was, therefore, not a case of “a man with a hammer looking for a nail,” but an attempt to solve an important real-world problem—like his previous invention of SOS.

For the epitaxial growth of GaAs, Manasevit merely adapted his Pyrex-tubing-based “SOS” epitaxial growth system for the growth of GaAs using metalorganic sources for Ga, e.g., trimethylgallium—TMGa [ $(\text{CH}_3)_3\text{Ga}$ ], and simple hydrides, e.g., arsine,  $\text{AsH}_3$ , for the column V element. One problem with this approach was that the “electronic-grade” metalorganic compounds (also known as metal alkyls or organometallics) he needed as the group III sources, e.g., trimethylgallium, trimethylindium—TMIn [ $(\text{CH}_3)_3\text{In}$ ], and trimethylaluminum—TMAl [ $(\text{CH}_3)_3\text{Al}$ ], were not commercially available. When Manasevit began his work on MOCVD growth of III–Vs on oxides, the chemical industry, e.g., the Ethyl Corporation of America,<sup>54</sup> and Texas Alkyls<sup>55</sup> were producing large quantities (i.e., metric tons) of “industrial-grade” trimethylaluminum,  $(\text{CH}_3)_3\text{Al}$ , for use as a catalyst in the organic chemistry industry, specifically, in the manufacture of polyolefins.<sup>56</sup> So when Manasevit called potential vendors to ask about purchasing organometallics, he was asked “How many railroad cars of chemicals do you want?”<sup>57</sup> As a consequence, Manasevit had to find industrial organometallic vendors who would be willing to create the necessary somewhat “unique” small-volume “high-purity” organometallic sources for his research. Some of the “custom chemical” suppliers Manasevit contacted who were willing to provide these materials were Alfa-Ventron, Orgmet, Research Organic Corp./Research Inorganic Corp. (ROC/RIC), and Texas Alkyls.<sup>15</sup> However, such chemicals were mostly “one-off” products made in small batches (50–100 g or less) on demand and not carefully analyzed for impurities, and each batch was different from the last. An additional problem was that the packaging used to deliver these highly reactive and pyrophoric compounds employed valves and fittings that were inherently leaky, leading to increasing oxidation of the metalorganic contents over time.

An additional challenge was to obtain adequately oriented and polished high-quality crystalline insulating oxide substrates, e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{MgAl}_2\text{O}_4$ , as well as other insulating crystals, e.g., diamond, that Manasevit was interested in using as substrates. In fact, once Manasevit traveled to the Los Angeles area “diamond district” to purchase diamonds to grow III–Vs on. However, when Manasevit heated one of his newly purchased “diamonds” in his reactor in  $\text{H}_2$ , he discovered that the “diamond” melted! When Manasevit called the vendor to report his experimental findings, the shocked diamond dealer became quite agitated and he politely asked Manasevit not to report this experiment and was provided with several “real” diamonds at no additional charge.<sup>58</sup> A photograph of Dr. Manasevit in front of the gas panel of one of his “Pyrex reactors” is shown in Fig. 1.

Under these circumstances, Manasevit’s early heteroepitaxial films were quite impure and also, being heteroepitaxial grown directly on oxides, contained a high density of defects. In spite of these difficulties, in 1969, Manasevit’s colleagues at Rockwell made the first MOCVD electronic devices—Schottky-barrier GaAs/sapphire field-effect transistors (FETs) with these radically “new” materials.<sup>59</sup> Their first report in a scientific journal was a 1969 paper by M. Waldner and I. D. Rouse, who fabricated these FETs from the GaAs/sapphire material grown by Manasevit.

While Manasevit studied the heteroepitaxial growth of a wide variety III–V and even IV–VI semiconductors on various insulating oxides by this process in the early and middle 1970s,<sup>38,60–66</sup> and other workers explored MOCVD growth on GaAs substrates in this period,<sup>67–71</sup> they were unable to demonstrate materials’ quality comparable to that of other competing and more developed III–V epitaxial materials technologies such as LPE and halogen-(chloride-) and hydride-based VPE.

In the period of 1967–1968 during which Manasevit was beginning his development of MOCVD, workers at Bell Labs and

other major labs were developing the epitaxial process for III–V semiconductors using “ultra-low-pressure (vacuum) molecular evaporation” that came to be called molecular-beam epitaxy (MBE). MBE also has a complex history.<sup>72,73</sup> MBE of III–Vs was first discussed by K. Günther at Siemens in 1958<sup>74</sup> and later demonstrated by J. E. Davey and T. Pankey at the U.S. Naval Research Lab in 1967<sup>75</sup> and by John Arthur and John LePore at Bell Labs in 1969.<sup>76</sup> MBE came into the extensive study after the publication of the initial MBE work of Alfred Yi Cho at Bell Labs in 1970.<sup>77</sup> Cho joined Bell Labs in 1968 after getting his Ph.D., studying the interactions of atoms with solid surfaces at the University of Illinois at Urbana-Champaign and was in the same group at Bell Labs as Arthur and LePore. Cho was the first to use the term “MBE,” and he demonstrated the epitaxial growth of GaAs and AlGaAs epitaxial layers in papers that appeared beginning in 1970. Later, in 1974, Cho and H. Craig Casey, Jr., reported the first pulsed 300 K operation of AlGaAs double-heterostructure (DH) laser diodes grown by MBE.<sup>78</sup> Two years later, in 1976, Cho *et al.* reported the first MBE-grown continuous-wave (CW) 300 K AlGaAs-GaAs DH lasers.<sup>79</sup> These results and further work on MBE by many others, in particular, the AlGaAs-GaAs superlattice work in 1973 and later by Leo Esaki, Leroy L. Chang, Raphael Tsu *et al.* at IBM Labs,<sup>80</sup> created an intense interest in MBE III–V epitaxial growth, and many research labs throughout the world began MBE research (if they could afford it). Furthermore, with the “Bell Labs and IBM Labs stamps of approval,” it was assumed that MBE was proper materials’ technology to replace LPE and VPE in the future. There was no need for any other “alternate” III–V epitaxial growth technology.

As a consequence of the competition by the “established” III–V epitaxial materials technologies, LPE and VPE, and the “designated semiconductor epitaxial technology of the future”—MBE, the research on MOCVD was practically stalled in the middle to late 1970s. In spite of the lack of commercial interest, Manasevit continued his MOCVD research on the growth of III–V heteroepitaxial layers on insulating oxide substrates, including Al-, In-, and Ga-containing compounds as well as the III-As, III-P, and III-N materials (see Refs. 37, 38, 60, and 61–66). Later, in 1975, he pioneered the growth of Sb-containing III–Vs<sup>81</sup> and IV–VI compounds<sup>66</sup> by MOCVD as noted above. Because Manasevit was primarily interested in the materials’ growth, structural properties, and crystallographic orientations of epitaxial III–Vs on insulators, his work was not recognized as much as it should have been. Today, of course, in 2023, the MOCVD III-N-on-sapphire materials technology dominates the violet, blue, green, and white LED markets world-wide and the (0001) sapphire insulating oxide substrates that Manasevit first employed dominate this market with 100–150 mm diameter sapphire substrates being used in large quantities for this purpose with >1000 MOCVD reactors in operation world-wide. This market is the dominant reason that there are so many MOCVD reactors working 24/7 on growing III-N materials. The value of the MOCVD-produced LED market in 2023 was estimated to be worth ~\$100 B with an estimated CAGR of 11.35% growing to ~\$171 B in 2028.<sup>82</sup> The MOCVD growth of GaN power electronic devices on 200 mm diameter Si wafers is also under development and is expected to add significantly to the volume and value of MOCVD materials produced each year by 2030.



**FIG. 1.** (a) Photograph of Hal Manasevit in front of one of his early Pyrex-tubing reactors in the 1960s. (b) Photograph of Hal in his office in about 1978. Specific dates unknown. Used with permission of the H. M. Manasevit family.

### III. EARLY MOCVD III-V DEVICES

As noted above, the first III-V devices of any kind fabricated from MOCVD-grown materials were GaAs/sapphire Schottky-barrier FETs reported in 1969, only one year after Manasevit's first publication on MOCVD.<sup>59</sup> By the early 1970s, hydride VPE dominated the production of GaAsP visible light-emitting diodes (LEDs) with Monsanto producing over 100 000 sq. in. per month of GaAsP epitaxial materials.<sup>83</sup> In addition, chloride VPE (using GaCl<sub>3</sub> and AsCl<sub>3</sub>) dominated the production of high-purity GaAs for electronic devices, e.g., metal-semiconductor field-effect transistors (MESFETs). In 1967, the LPE process for the growth of Al<sub>x</sub>Ga<sub>1-x</sub>As alloys was reported by Hans Rupprecht *et al.* at IBM Labs.<sup>84</sup> By the early 1970s, LPE was the dominant epitaxial materials' technology for many III-V heterojunction materials, especially Al-containing devices, including AlGaAs LEDs,<sup>85</sup> DH lasers<sup>86,87</sup> solar cells,<sup>88</sup> and other heterojunction devices.<sup>89</sup> By 1975, MBE was being actively researched by a few large industrial and government research labs (only they could afford it), particularly, e.g., at the two major U.S.-based research laboratories, Bell Labs<sup>90,91</sup> and IBM Research Laboratory,<sup>73,92,93</sup> the Mullard Research Labs, UK,<sup>94</sup> and in the Electrotechnical Laboratory, Japan.<sup>95</sup> Consequently, the future seemed to be for MBE to take over the III-V epitaxial world.

However, in 1975, Yasuo Seki *et al.*, from Nippon Electric Company, Ltd. (NEC) in collaboration with Sumitomo Chemical Co. in Japan, reported on relatively high-purity GaAs films grown by MOCVD on Si- and Cr-doped (100) GaAs substrates using "high-purity" triethylgallium (TEGa) and AsH<sub>3</sub>.<sup>96</sup> These films exhibited net free-electron concentrations as low as  $n \sim 7 \times 10^{13} \text{ cm}^{-3}$  and Hall mobilities  $\mu_n \sim 120\,000 \text{ cm}^2/\text{Vs}$  at 77 K for MOCVD GaAs films  $\geq 10 \mu\text{m}$  thick grown on Cr-doped GaAs substrates. At the time, these were deemed remarkable results and nearly equal to that of the current State-of-the-Art "high-purity" GaAs films grown by the "standard" GaCl<sub>3</sub>-AsCl<sub>3</sub>-H<sub>2</sub> chloride VPE process. Although Manasevit's earlier work on using TEGa to grow heteroepitaxial GaAs on sapphire employed relatively low-purity TEGa,<sup>38</sup> the NEC team's organometallics had been supplied as specially purified TEGa from Sumitomo Chemical Company, and this higher-purity ethyl-based Ga source reduced the concentrations of both oxygen and carbon unintentional films in the homoepitaxial GaAs epitaxial layers. These results pointed the way for MOCVD to be developed further. Things were beginning to change.

As discussed above, Manasevit had demonstrated the power of MOCVD to grow Al-containing III-V semiconductors in 1971.<sup>62</sup> This capability was lacking for the conventional halide and halogen (chloride) VPE III-V growth technologies so the devices composed of Al-containing III-Vs (mostly Al<sub>x</sub>Ga<sub>1-x</sub>As-GaAs laser diodes with  $x < 0.30$ ) were universally grown commercially by LPE. In addition, many laboratories were studying MBE growth for AlGaAs alloys and, in fact, for the growth of ultrathin AlGaAs-GaAs heterostructure multiple-layer superlattices.<sup>97</sup> In the 1970s, the primary commercial interest in Al-containing III-V optoelectronic devices was for AlGaAs DH laser diodes<sup>98</sup> for telecommunications and high-efficiency AlGaAs-GaAs heterostructure solar cells.<sup>99,100</sup> Both of these Al-containing III-V devices required high-quality materials and heterostructures with long minority-carrier lifetimes and low concentrations of defects and impurities for optimal performance.

In fact, for some applications, the optimized AlGaAs-GaAs solar cell required high-quality Al<sub>x</sub>Ga<sub>1-x</sub>As wider-bandgap "window" layers with the relatively high [Al]  $x \sim 0.65$ !<sup>100</sup>

The interest in Al<sub>x</sub>Ga<sub>1-x</sub>As-GaAs laser diodes was largely driven by the need for a compact, low-cost, highly reliable source of coherent near-infrared light at  $\sim 850 \text{ nm}$  for the first-generation of fiber-optic telecommunications and was under active study and development in many laboratories throughout the world in the 1970s. As a result, the capability of growing on large-area substrates was considered to be an important characteristic of the required production-scale epitaxial materials growth technology. Most of the LPE systems being used at that time for AlGaAs growth were limited to using  $\sim 2 \text{ in.}$  diameter substrates, but some systems could employ two to four such substrates in one run. However, the epitaxial layer uniformity within a wafer and within a run was poor, and consequently, device yields were generally low. This caused such LDs (and AlGaAs-GaAs heterostructure solar cells) to be quite expensive. This was an especially important problem for the production of AlGaAs-GaAs heterostructure solar cells where large-area devices were required for the highest power performance. Clearly, another III-V epitaxial materials growth solution was needed, and that is where the MBE technology was destined to become a dominant player—or so it was thought. However, the question remained, could MOCVD be improved enough to make an AlGaAs DH laser diode or a high-efficiency AlGaAs solar cell? If so, the already demonstrated advantages of VPE in the large-scale production of III-V materials could be harnessed to make such devices over large areas and at lower cost than either LPE or MBE.

#### A. My initial work on MOCVD homoepitaxial semiconductor device growth

This was a critical issue that I began to study when, in February 1975, I was hired by Jack Mee, the acting Group Leader of the group Manasevit, and his assistant, William I. Simpson, worked in what was by then called the Rockwell International Electronics Research Center in Anaheim, CA.<sup>101</sup> My initial assignment was to study the electrical and optical properties of MOCVD-grown III-V materials. I started work by setting up a photoluminescence system for III-V materials' characterization. For this purpose, I ordered a new Ar-ion laser, photomultiplier, picoammeter, etc. While waiting for this equipment to arrive, I spent a few months studying the electrical properties of GaAs/sapphire heteroepitaxial films grown by Manasevit and Simpson using an MOCVD reactor that Simpson had designed and built in the Rockwell Anaheim MOCVD Lab.

In my graduate-school days, working on my Ph.D. with Professor Nick Holonyak, Jr., at the University of Illinois at Urbana-Champaign, I had experience with the growth of a variety of III-V materials, e.g., the solution growth of InGaP and the LPE growth of GaAs, AlGaAs, and AlGaAsP. Furthermore, I also had some indirect knowledge of the VPE growth of GaAsP alloys from experiences gained during my Ph.D. studies, where I had worked with VPE GaAsP crystals grown by George Craford's team at Monsanto. I realized that the MOCVD process could do something unique—it could provide a VAPOR PHASE source of Al!

This important capability intrigued me and was a prime reason I decided to work on MOCVD growth as well as on characterization and device fabrication. This would produce a direct method to provide the quick “feedback” necessary to improve the materials’ quality necessary to make AlGaAs–GaAs heterojunction devices and LDs in particular.

As noted above, Manasevit was primarily interested in the heteroepitaxial growth of III–Vs on single-crystal oxides. However, I wanted to study the properties of III–V materials grown on native single-crystal substrates, e.g., GaAs. Since Hal was not interested in this and in order for me to have control of the materials I would be characterizing, I decided to build an MOCVD reactor system myself to study the growth of heteroepitaxial and homoepitaxial III–V films and device structures. I was very familiar with this “grow and characterize” mode of materials and device research, since during my M.S. and Ph.D. research in Holonyak’s lab, we had built much of our own crystal-growth apparatus, even to the point of winding our own Kanthal® furnace heater elements. Consequently, I already had some prior experience in building crystal-growth systems in Holonyak’s lab. In addition, after receiving my Ph.D. in 1973, I worked in the Optoelectronics Group of the Semiconductor Division of Texas Instruments, Inc., Dallas, TX, on the LPE growth of N- and Zn-O-doped GaP LEDs. There I built a new large-scale LPE system with a gas panel capable of growth on three 2.0 in diameter wafers for the development of GaP:N green (using ammonia as an N source) and GaP:Zn–O red LEDs, providing me some additional experience in the design and fabrication of “industrial” semiconductor epitaxial growth systems.

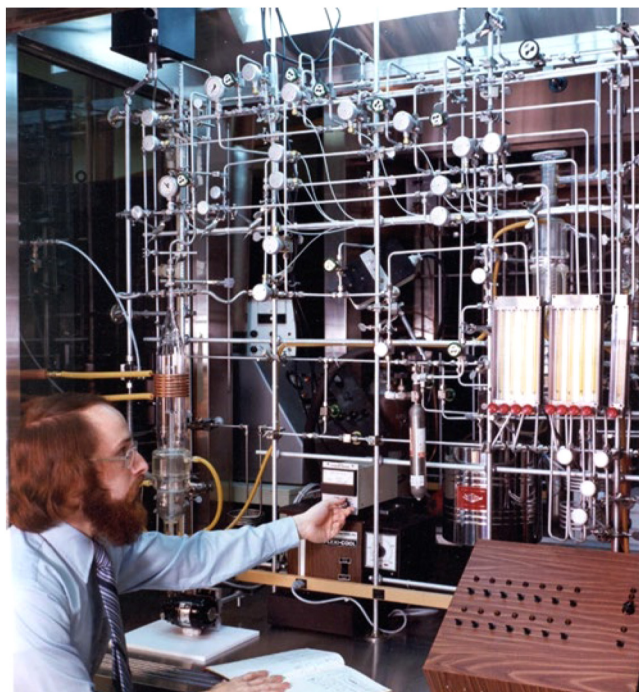
I started building my first MOCVD reactor at Rockwell in the summer of 1975 with a very small budget, largely using recycled valves, fittings, rotameters, oil-based vacuum roughing pumps, pressure gauges, etc., as well as partially used TMGa sources, that Manasevit and Simpson had used in earlier experiments.<sup>16,102</sup> I had to “re-clean” and “reclaim” almost all of these fittings and valves that I had scrounged from the used-parts bins and most of these components employed either standard Swagelok® tube or pipe-thread connections. In fact, the MO sources I used in these first MOCVD growth experiments were “previously used” sources in leaky bubblers that had, in some cases, been stored in a simple unvented solvent cabinet placed outside near the parking lot of the Anaheim research lab and subject to all the heat, cold, and humidity of several California summers and winters. My MOCVD reactor system’s basic features, e.g., a quartz vertical-chamber, atmospheric-pressure growth (now referred to as AP-MOCVD), RF heating, slow graphite susceptor and wafer rotation, followed the design that Manasevit had been using since at least 1967, including the use of a Pyrex-glass Hg-vapor high-vacuum pump combined with a quartz liquid nitrogen trap for removing the air and water vapor from the growth chamber prior to a growth run. In addition, during several design “upgrades,” I took particular care with the reduction of the “dead space” of the gas piping system for fast gas switching as well as the cleanliness and the assembly of the components to ensure that the system was as clean and leak-tight as possible. I knew that this would be critically important in the handling and use of highly reactive Al-containing alkyl compounds. However, we did not have access to a He mass-spectrometer leak detector, so all the reactor

system was tested using the “vacuum pressure rise versus time” test using the Hg-vacuum pump and standard thermocouple vacuum gauges.

Since I was interested in growing AlGaAs–GaAs DH lasers to demonstrate the properties of MOCVD devices, I designed and built a fast-switching “vent-run” gas manifold for gas injection at the input of the growth chamber and an electronic control system to allow me to switch several valves at one time, allowing me to grow “abrupt” heterojunctions and doping profiles—or so I hoped. After the reactor was completed, I initiated a growth parameter study of the III/V ratio, total flow rate, growth temperature, etc., to optimize the electrical properties of the GaAs and AlGaAs doped films as well as the 300 K photoluminescence intensity of the AlGaAs layers and “test” DHs. Another parameter I studied was the flow dynamics of the chamber at different total gas flow rates by examining the deposits that occurred on the inner wall of the reactor tube somewhat above, near, and below the susceptor during growth. Other features were the location and size of the small quartz disk (that we referred to as a “ducat” since it was about the size of the famous Venetian coin) as a gas deflector on the vertical injection tube that was positioned at the gas entrance of the reactor. While I eventually was able to purchase an Alcatel chemical series roughing pump for reactor evacuation, I did not have any pressure control system or any way to control the pressure in the bubblers to allow the chamber pressure to be varied during growth.

By October 1975, I had a working GaAs AP-MOCVD system for the growth of GaAs *p-n* junctions fitted with metalorganic bubbler sources of “hand-me-down” TMGa and diethylzinc (DEZn) for *p*-type doping and the hydrides AsH<sub>3</sub> (as a mixture of 10% AsH<sub>3</sub> in H<sub>2</sub>) as well as H<sub>2</sub>Se for *n*-type doping (as ~200 ppm mixture in H<sub>2</sub>). A photograph of one early incarnation of this first MOCVD reactor (I called “Reactor A”) taken in October 1975 is shown in Fig. 2. During the 1975–1976 time frame, I continued to add capabilities to this MOCVD reactor, e.g., improving the gas-switching system using bellows-sealed stainless steel low-dead space Tylan® three-port pneumatic valves and adding a bubbler of TMAI and I continued my studies of the *n*-type and *p*-type doping of GaAs and AlGaAs using the Se and Zn sources, respectively. Much of this early calibration work was performed using (0001) sapphire substrates, which I could reuse by etching off the previously grown film, greatly reducing the cost of the research. Occasionally, I would use an “expensive” Cr-doped (100) GaAs substrate to provide a more relevant calibration of materials’ electrical properties that did not include the defects inherent in the heteroepitaxial growth of GaAs on sapphire.

In 1975 (the same year as Seki’s first work was published<sup>96</sup>), Sydney J. Bass at the UK Services Electronics Research Laboratory (SERL) in Baldock, Hertfordshire published a study of GaAs epitaxial layers grown by MOCVD on Cr-doped GaAs substrates using a small horizontal-geometry RF-heated reactor chamber and TMGa and AsH<sub>3</sub> sources.<sup>103</sup> This reactor chamber—known in the United Kingdom as the “Bass Cell”—was to become a standard for early commercial MOCVD reactors manufactured in the United Kingdom. Bass found that the background doping of the undoped films could be *n*- or *p*-type with 300 K net electron concentrations as low as  $n = 5 \times 10^{15} \text{ cm}^{-3}$  and 300 K electron mobilities as high as



**FIG. 2.** R. D. Dupuis at the controls of one early incarnation of his first MOCVD reactor at Rockwell International, Anaheim, CA. The TMGa bubbler is visible near the center. Photograph taken on October 20, 1975. I called this system “Reactor A” after my second MOCVD system (Reactor B) was completed. Reproduced with permission from R. D. Dupuis, IEEE J. Sel. Topics Quant. Electron. **6**, 1040 (2000). Copyright 2000, IEEE.

$\mu_n = 6260 \text{ cm}^2/\text{V s}$ . Using low-temperature photoluminescence, he found that carbon and small concentrations of Zn were the primary impurities in undoped films. A year later, in 1976, White *et al.*,<sup>104</sup> at the Royal Radar Establishment (RRE) in Malvern, Worcestershire, reported that a comparison of deep-level traps in LPE, VPE, and MOCVD-grown GaAs films on GaAs substrates showed that the MOCVD films had a larger concentration and wider variety of electron traps than similar films grown by LPE and VPE. In fact, it was widely reported that III-V films grown by MOCVD had large concentrations of unintentional impurities, including carbon and oxygen, which created deep levels that limited the mobility of carriers.

This work on homoepitaxial growth of GaAs emphasized that better purity in the MOCVD-grown films was needed. Consequently, I decided that besides designing and building a “leak-tight” reactor, I needed to improve on the packaging of MO sources by replacing the “leaky” 304-stainless-steel bubblers provided by the vendor<sup>105</sup> with custom-made all-welded 316-stainless-steel bubblers of my own design. Note that the first version of Reactor A shown in Fig. 2 (near the center of the photograph) has a “standard” vendor-supplied 304 SS TMGa bubbler with Teflon taped pipe-thread fittings and simple packed valves, all of which were “leaky.” I had my new metalorganic source cylinders fabricated

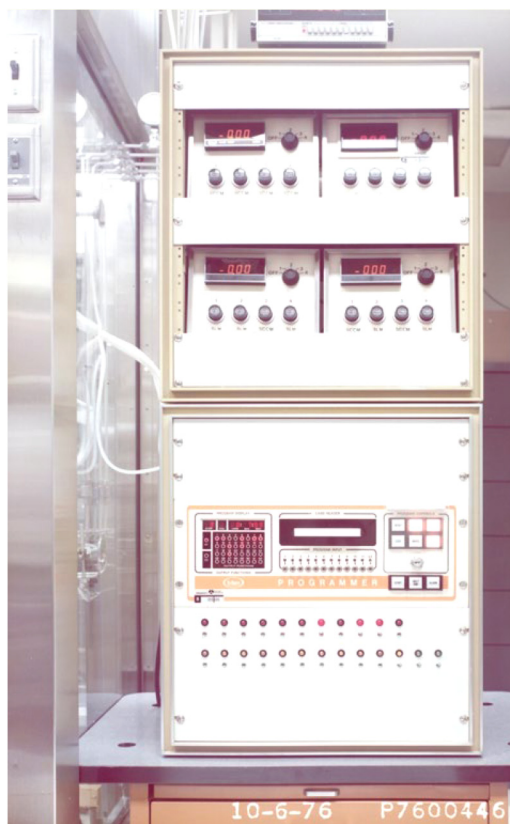
from components that I designed and had machined at Rockwell. After I cleaned them, I had these special 316 SS components and all-welded Nupro® Model SS-4H bellows-sealed valves assembled and welded using electron-beam welding so that the alkyls would stay as pure as possible while they were used.<sup>106</sup> After the MO sources were delivered, I transferred the commercially supplied alkyls from the “leaky” bubblers in which they were packaged into these UHP bubblers using a high-vacuum transfer procedure. To my knowledge, these are the first high-purity all-welded metalorganic source containers ever used. I think this change in packaging was especially important since (in my case) the TMGa bubblers were immersed in a vacuum dewar filled with an ice and water bath, while the TEGa and TMAI bubblers were just left in “room air” for temperature control (we had no constant-temperature baths for this purpose at Rockwell) so the vendor-supplied bubblers, with their “pipe-thread-sealed fittings,” were in water or in air virtually all the time so Teflon-tape-sealed pipe threads were to be avoided.

By early 1976, I had developed enough growth calibration results to begin to work on the study of GaAs *p-n* junctions and AlGaAs-GaAs heterojunctions on (100) *n*-type GaAs substrates. The *I-V* characteristics of these first GaAs *p-n* junctions looked surprisingly good on the curve tracer, so I decided to expose the wafer to illumination from a microscope light and I saw a large photoresponse. During 1976, using internal Rockwell funds, I continued to improve the design of Reactor A by adding electronic mass flow controllers to replace the “Rotameters” and an electronic switching system to replace the simple “switch box” as shown in Fig. 3. During the Spring of 1976, I had grown AlGaAs-GaAs *p-n* junction solar-cell heterojunctions, and after processing the first wafers, I discovered an even stronger photovoltaic response than before. I further evaluated these first solar-cell devices outside in the Rockwell parking lot to get some idea of the uncalibrated “air-mass 1.5” photoresponse. Even with primitive contact designs, the photoresponse seemed excellent.

A year after I joined Rockwell, in 1976, Dr. P. Daniel Dapkus was hired from Bell Labs to the Group Leader position of our small MOCVD group. The success of my initial work on MOCVD AlGaAs-GaAs solar cells allowed me, Manasevit, Dapkus, Dr. Ralph Ruth, and other colleagues to submit a proposal in 1976 to the U.S. Government’s ERDA<sup>107</sup> for additional funding for photovoltaic research to use MOCVD to grow low-cost III-V heterojunction solar cells on various metals and metal/glass composites. Using these funds, combined with additional Rockwell Internal Research and Development (IR&D) funding, I was able to further upgrade Reactor A and build an entirely new MOCVD reactor (I called Reactor B) with all new components and an improved design for the gas panel. I built this system in late 1976, and it was operational in early January 1977. A photograph of this reactor taken on January 14, 1977, is shown in Fig. 4.

This atmospheric-pressure MOCVD system employed a mixture of Swagelok® tube fittings with gold-plated ferrules<sup>108</sup> and Nupro® VCR® tube fittings with gold-plated SS or Ni gaskets as well as Nupro 316 SS bellows valves including Model SS-4H all-welded manual valves, Model SS-4BK-NC pneumatically actuated bellows valves and injection, a manifold composed of four Tylan® low-dead-volume three-port switching bellows valves, Tylan® Model





**FIG. 3.** A photograph taken October 6, 1976 of the electronic control panel of my first Rockwell MOCVD reactor (Reactor A) after I upgraded the flow control and valve switching systems. The upper cabinet contains the Tylan® FC-260 mass-flow-controller readouts and in the lower cabinet is the Tylan Tymer 16® Optical Programmer with optical IBM punch card reader that controlled all of the major pneumatically controlled Nupro® bellows-sealed stainless-steel valves. This is probably the first “computer-controlled” MOCVD reactor ever built.

FC-260 electronic mass flow controllers,<sup>109,110</sup> and a Tylan® computer-based controller that was programmed using an IBM-punch-card optical reader for program input. This controller could switch up to 32 outputs and store valve switching settings for 16 independent steps with an automatic “roll-over” repeating cycle. The gas flow rates, however, had to be set and changed manually using the individual MFC controls. Note that this system still employed a quartz chamber with a Cajon® Ultra-Torr O-Ring seal to the quartz inlet tube. It had a vacuum-grease-sealed ground-glass seal rotation feed-through and a ground-quartz reactor-base sealed with vacuum grease. At least these “low-tech” greased components were all down-stream in the exhaust side and not in the growth zone.

In addition to providing some funding for my MOCVD Reactor B, the ERDA project permitted me to hire Donald Yingling as my research technician to run Reactor A in late 1976. Yingling had worked with me earlier on LPE growth of GaP

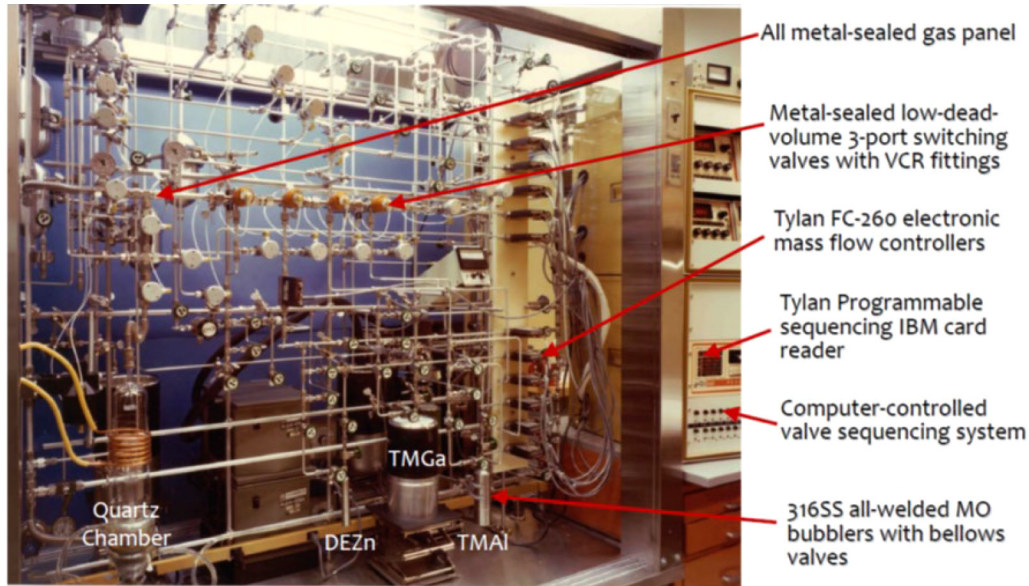
LEDs at Texas Instruments in Dallas, so he was very familiar with III–V semiconductors. In about 1979, Yingling left Rockwell to join the Xerox Palo Alto Research Center (PARC) and started working with Robert Burnham, Donald Scifres, and William Streifer and—using his new knowledge of MOCVD—helped set up the first MOCVD reactor at PARC to grow AlGaAs laser diodes. Subsequently, using this MOCVD reactor, they developed high-power LDs and emitter arrays using MOCVD growth for laser printers and pumping erbium-doped fiber amplifiers (EDFAs).<sup>111,112</sup> In 1983, Xerox and Spectra-Physics established a new start-up company, Spectra Diode Laboratories Inc. (SDL), to exploit the new high-power LD MOCVD technology developed at PARC.<sup>113</sup> SDL subsequently became the first company to exclusively exploit the power of MOCVD to create high-value laser diode products for commercial and government use. Based upon this MOCVD and LD expertise, SDL became one of the fastest growing companies in the fiber optics and optoelectronics industries in the United States and manufacturer of the world’s highest power semiconductor lasers at that time. In 2000, during the “telecom boom,” JDS Uniphase Corporation acquired SDL for \$41 B, which was reported to be the largest takeover offer ever for a high-technology company at that time.<sup>113</sup> MOCVD had indeed created a lot of value! This company is now part of Lumentum Inc., a world-leader in MOCVD LD and VCSEL technology.

### B. First MOCVD laser diodes and solar cells

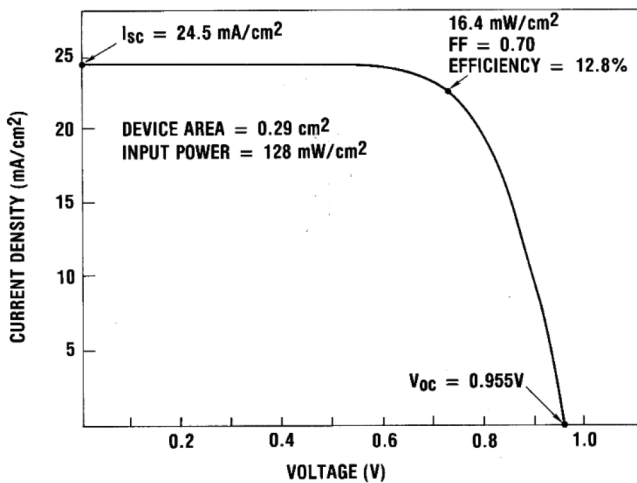
Using this second system, Reactor B, in April 1977, I grew new AlGaAs-GaAs *p-n* single-heterojunction solar cell wafers, fabricated  $1 \times 1 \text{ cm}^2$  solar cells, and tested them under simulated Air-Mass 0 conditions using the new solar-simulator equipment we were able to purchase using the ERDA funding. While these cells lacked antireflection coatings, these first test results were excellent as shown in Fig. 5, so I wrote up the data and submitted it for publication.<sup>114</sup> These were the first reported MOCVD-grown heterojunction devices and were the first that had a performance rivalling that of similar LPE-grown devices and, I am told, many people were surprised to read that an AlGaAs-GaAs solar cell, which is very sensitive to minority carrier transport properties and interfacial defects at the heterojunction, could be produced by MOCVD. A photograph of one of my first AlGaAs-GaAs solar cells is shown in Fig. 6. In May 1977, I submitted these first MOCVD solar cell results for presentation at the upcoming 1977 *IEEE Solid-State Device Research Conference* (commonly called the “DRC”—a conference series still held today<sup>115</sup>) to be held in June 1977 at Cornell University in Ithaca, NY.

With the success of the AlGaAs-GaAs solar cell growth, I knew that I had a good chance of making AlGaAs-GaAs DH laser diodes using MOCVD. So early in 1977, I started to use the new MOCVD Reactor B to study the growth of these double heterostructures and developed doping, alloy composition, and thin layer structure needed to accomplish this goal using essentially the same DH device design as was being grown by LPE. In early May 1977, I grew and processed my first complete LD wafer and the very first devices worked under pulsed excitation at 300 K—typical electroluminescence emission spectra are shown in Fig. 7. A photograph of the first MOCVD broad-area laser diode chip is shown in Fig. 8.

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**FIG. 4.** Photograph, taken on January 10, 1977, of Reactor B, the second MOCVD system, I built at Rockwell International in 1976–1977. This system used electronic mass flow controllers and computer control of the valve switching similar to the upgraded Reactor A. The “temperature control” for the TMGa source is the ice bath visible in the front center. The TMAI (on the right) and DEZn (on the left) sources were used at room temperature without any special temperature control—except the room air-conditioning. The custom-made all-e-beam-welded 316 SS bubblers are visible for the TMAI and DEZn sources. Note the “three-finger” tubing clamps typical of the earlier “Pyrex-glass-tubing” reactors. This made reactor piping systems relatively easy to modify. Not shown is the optical pyrometer used for the susceptor temperature readout. There was no actual real-time process temperature control. Reproduced with permission from R. D. Dupuis, IEEE J. Sel. Topics Quant. Electron. 6, 1040 (2000). Copyright 2000, IEEE.



**FIG. 5.** J-V photoresponse of one of the first MOCVD-grown AlGaAs-GaAs solar cells (no AR coating) taken at 300 K. This small-area device ( $\sim 0.29 \text{ cm}^2$ ) was tested using a solar simulator having an AM0 spectral output. This figure shows the inverted Quadrant 4 of the J-V characteristic. After (Ref. 114). Reproduced from R. D. Dupuis *et al.*, Appl. Phys. Lett. 31, 201 (1977). Copyright 1977, AIP Publishing LLC.

This device was mounted *n*-side down and had two wire bonds to the *p*-side. This laser diode chip had four cleaved facets because I was in a hurry to test the laser performance, so I did not bother doing any sawing of the sides of the first chips—I just cleaved all the facets. Almost as soon as I had the laser data, I wrote up the manuscript and submitted it to *Applied Physics Letters*.<sup>116</sup> Subsequently, our improved laser diodes employed oxide-defined narrow-stripe *p*-contacts for CW operation.

After I submitted these results for publication, I also submitted an abstract to the 1977 DRC Program Committee as a “Late News Paper” describing these first MOCVD DH laser diode results. However, I would not know if my Late News Paper abstract was accepted until I actually got to the meeting! When I arrived in Ithaca on Sunday afternoon prior to the start of the meeting, I met with my Ph.D. advisor, Professor Nick Holonyak, Jr., who was also giving some papers at the conference. I learned from Professor Holonyak, who was on the conference’s Program Committee, that my LD abstract was accepted for presentation as a “Late News Paper.” However, later I met Dr. Richard Dixon (from Bell Labs, Murray Hill, NJ) who was also on the Program Committee, and he told me that the paper was accepted with the expressed condition that I “Tell all about how the results were achieved.” I gave my Late News Paper in a very full conference room, and there were lots of questions about the details of how this work was performed.<sup>117</sup> I

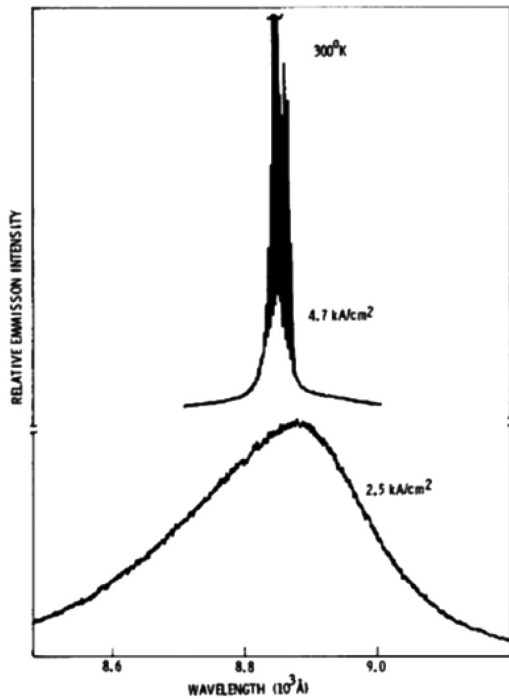
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**FIG. 6.** Photograph of one of the first AlGaAs-GaAs “window” solar cells grown by MOCVD in 1977. The longer dimension of the device is  $\sim 1$  cm. A simple “grid” contact pattern was used for this device. We subsequently developed a  $1 \times 1$  cm<sup>2</sup> device with an improved the top ohmic contact design for higher efficiency.



**FIG. 8.** Optical micrograph of the first MOCVD AlGaAs-GaAs broad-area DH laser diode taken on May 26, 1977. The device size was  $800 \times 800 \mu\text{m}^2$  and was mounted *n*-side down, and the two visible wire bonds were made to the *p*-GaAs:Zn contact layer. This chip had four cleaved Fabry-Perot facets. This device was operated under pulsed conditions at 300 K a few days before this photograph was taken on May 26, 1977.



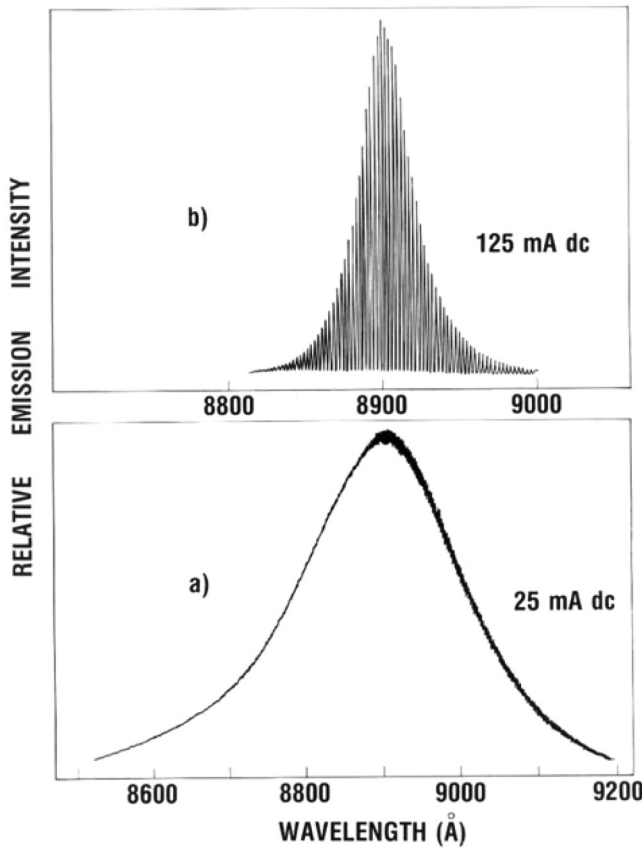
**FIG. 7.** Pulsed electroluminescence spectra at 300 K of an early MOCVD AlGaAs-GaAs broad-area DH laser diode below and above laser threshold. The threshold current density was  $J_{th} \sim 4.2$  kA/cm<sup>2</sup>. Reproduced from R. D. Dupuis and P. D. Dapkus, *Appl. Phys. Lett.* **31**, 466 (1977). Copyright 1977, AIP Publishing LLC.

merely answered, “With great attention to detail!”<sup>118</sup> I could tell there was lots of excitement about this report, but there were also lots of skeptics as well. Many of the skeptics were finally convinced later in 1977 when our paper on DH LDs with AlGaAs-based active regions was published.<sup>119</sup> In that work, we were first to demonstrate MOCVD DH LDs with  $\text{Al}_y\text{Ga}_{1-y}\text{As}$  ( $0.08 < y < 0.12$ ) active regions, and emitting at wavelengths short as 804 nm, proving that MOCVD AlGaAs was of high quality. Furthermore, in April 1978, we published the first paper on the CW 300 K operation of MOCVD-grown AlGaAs-GaAs lasers,<sup>120</sup> as shown in Fig. 9. Finally making it clear to all that MOCVD was a powerful technology for the growth of III-V optical devices.

#### IV. MOCVD HETEROSTRUCTURES AND QUANTUM-WELLS

At this same DRC in June 1977, Professor Holonyak gave a Late News Paper describing for the first time the growth of III-V laser diodes with multiple ultrathin heterostructure layers in the active region that exhibited “quantum-size effects” (QSE) in the emission spectra.<sup>121</sup> This was a big surprise that shocked many because this first successful laser diode fabricated using active regions exhibiting ultrathin QSE was realized using low-cost LPE and was NOT grown in an expensive MBE system! This first demonstration of QSE laser diodes was later published in August 1977.<sup>122</sup> Another surprising aspect of this report was that these

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**FIG. 9.** 300 K emission spectra for one of the first MOCVD-grown CW DH LDs below (a) and above (b) threshold. The threshold current density for this  $\sim 14 \times 380 \mu\text{m}^2$  mesa-stripe-geometry laser diode is  $\sim 2.25 \text{ kA/cm}^2$ . Reproduced from Dupuis *et al.*, *Appl. Phys. Lett.* **32**, 295 (1978). Copyright 1978, AIP Publishing LLC.

QSE-LDs were not created from “simple” lattice-matched AlGaAs-GaAs thin layers but from thin layers composed of the more complex and difficult to grow quaternary InGaPAs-InP system, which is not intrinsically lattice-matched like AlGaAs-GaAs! Previously, a few BTL and IBM researchers had reported on the low-temperature electrical<sup>123</sup> and optical properties of MBE-grown multiple “ultrathin” AlGaAs-GaAs heterostructures,<sup>124,125</sup> and Raymond Dingle and Charles H. “Chuck” Henry at BTL even patented an LD with such an active region.<sup>126</sup> However, no *room-temperature* lasers of any kind—either optically or electrically pumped—had been reported from such MBE-grown QSE heterostructures. In fact, at this time in 1977, the most recent of these reports only showed the operation of low-temperature optically pumped lasers (not injection laser diodes) with many ( $\sim 50$ ) pairs of layers and that the laser thresholds for such multiple-layer thin heterostructures were much higher than for “conventional” AlGaAs-GaAs DH materials grown by LPE.<sup>125</sup> Furthermore, no other materials technology besides MBE was believed to be capable

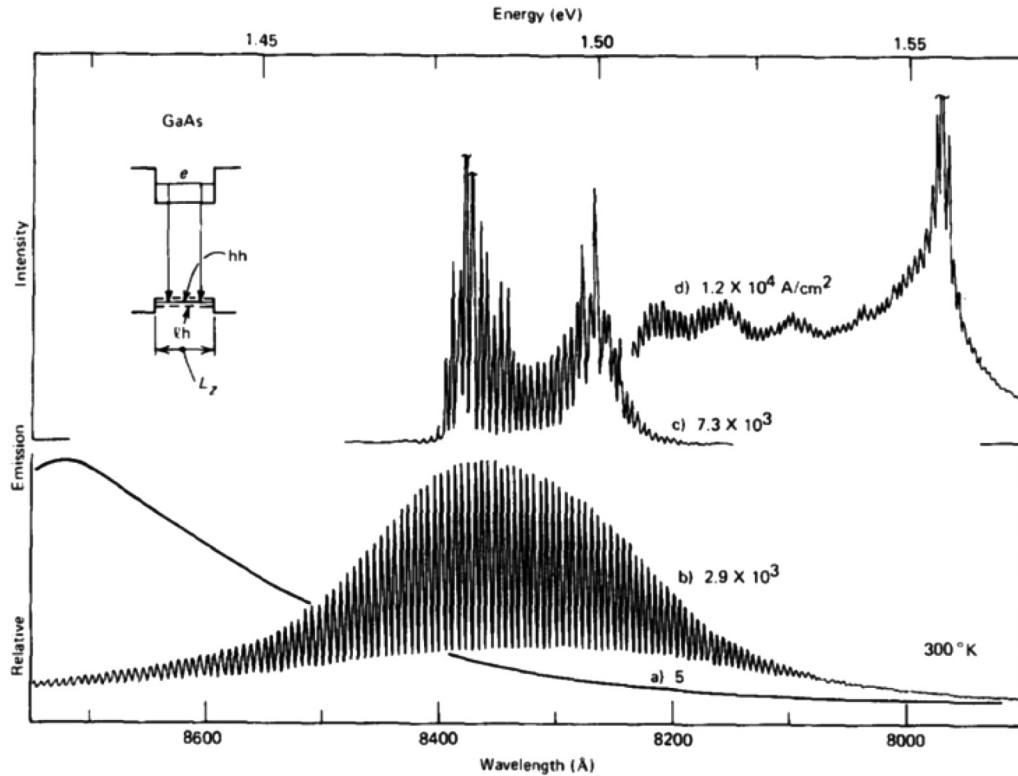
of making such ultrathin III-V semiconductor layers uniformly and reproducibly.<sup>127</sup> Holonyak’s LPE-grown QSE lasers were not only the first non-AlGaAs-based lasers exhibiting QSE—they were also the first QSE lasers not grown by MBE—and in fact they were also the first QSE diode lasers—now universally known as “quantum-well laser diodes—QW LDs.”<sup>128</sup>

In my informal Sunday afternoon meeting with Professor Holonyak prior to the beginning of the conference, we discussed our “Late News Paper” results, and I described in some detail the design of my Reactor B with its computer control. Professor Holonyak was amazed since he had been trying to get Monsanto (whom he consulted for) to set up such a hydride VPE system to grow ultrathin layers of III-V semiconductors, but they did not want to devote any effort to this because the commercial production demands of developing and producing red, orange, and yellow GaAsP LEDs were keeping everyone busy—also, they had no way to incorporate Al in order to maintain lattice matching in their GaAsP HVPE systems. Holonyak and I began a discussion of how to collaborate on the use of MOCVD for the growth of ultrathin AlGaAs-GaAs heterostructure lasers. After the conference ended in late June, I returned to my lab and immediately began working on the growth of multiple-quantum-well (MQW) LDs. This collaboration with Holonyak quickly bore fruit, and four months later, we had demonstrated the first “quantum-well” (QW) injection laser diodes (these diodes had a single QW of  $\sim 20 \text{ nm}$  thick) operating at 300 K in the pulsed mode, as shown in Fig. 10 (Refs. 129 and 130), and then a short time later, MQW optically pumped lasers operating CW at 300 K,<sup>131</sup> then CW MQW injection lasers at 300 K,<sup>132</sup> and CW single-QW LDs at 300 K in October 1978.<sup>133</sup> In fact, the term “quantum-well laser” was first used to describe these MOCVD-grown LDs with ultrathin active regions.<sup>134</sup> With the demonstration of MOCVD AlGaAs-GaAs QW lasers, we expanded our research to study the interaction of phonons with the photon population in the QWs and published several papers on this with Holonyak and his team at UIUC.<sup>135–137</sup> One example of this work is shown in Fig. 11.<sup>137</sup>

It is interesting to note that the first MBE-grown MQW LDs were not reported until over one year later in 1979 by Won-Tien Tsang *et al.* at Bell Labs, but these lasers had high threshold current densities and only operated pulsed at 300 K.<sup>138</sup>

At this same 1977 DRC, I also presented our “regular paper” describing our work on MOCVD-grown AlGaAs-GaAs heterojunction solar cells.<sup>139</sup> This report actually was the first to describe a high-performance MOCVD-grown III-V device and was published a few months before the LD results in 1977.<sup>114</sup> Interestingly, the MOCVD LD results created much more interest than the MOCVD solar-cell results, even though the solar cell is in some ways more sensitive to defects since long minority-carrier diffusion lengths and high-quality heterojunctions are required for high efficiency at AM0 than is the threshold current density of the majority-carrier dominated LED and LD.<sup>140</sup> At the time, LPE was the only technology employed for the growth of high-efficiency III-V single-heterojunction solar cells, and the substrate area was limited to about a few 2 in. diameter GaAs wafers. In this paper on MOCVD-grown AlGaAs-GaAs heterojunction solar cells (the first paper I published on MOCVD grown devices), I stated that MOCVD could potentially be scaled up to grow complex

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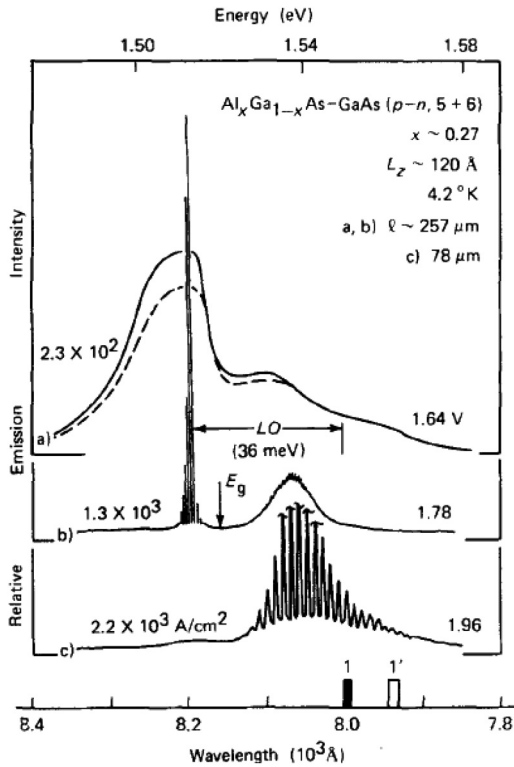
**FIG. 10.** Pulsed 300 K electroluminescence spectra of one of the first quantum-well laser diodes to operate at room temperature. The diodes employed an AlGaAs-GaAs single-quantum-well active region grown by AP-MOCVD. The curves (a)–(c) are for a diode with a cavity length of  $\sim 170\ \mu\text{m}$  long. The threshold current density was  $J_{\text{th}} \sim 3 \times 10^3\ \text{A/cm}^2$ . Curve (d) is for a different diode. Reproduced from Dupuis *et al.*, *Appl. Phys. Lett.* **32**, 295 (1978). Copyright 1977, AIP Publishing LLC.

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heterostructures on substrate areas as large as  $\sim 200\ \text{cm}^2$  in a single run, a potentially great advantage for the growth of lower-cost high-efficiency solar cells and LEDs. This landmark performance was exceeded  $\sim 40$  years later, as only one example, when AIXTRON developed the AIX G5 + C Planetary MOCVD reactor system with a capacity of five each 8 in. (200 mm) diameter substrates or a total substrate area of  $\sim 300\ \text{cm}^2$  per run.<sup>141</sup> Today, all of the production and research of such advanced high-performance III-V solar cells are performed using MOCVD.<sup>142</sup> In fact, the properties of MOCVD have allowed the development of the highest-performance multiple-junction III-V solar cells as shown in the upper curves of Ref. 142. Some recent examples of the highest-efficiency triple-junction III-V non-concentrator solar cells grown by MOCVD have a power conversion efficiency of 35.9%–39.5% at AM 1.5 g and are discussed in Refs. 143 and 144.

The demonstration that MOCVD could be used to precisely grow multiple-thin-layer heterostructures, i.e., MQWs, having layers as thin as those produced by MBE was a great surprise to many.<sup>145</sup> In several instances, reviewers of our manuscripts and others at conferences who were skeptical wanted proof that the MOCVD-grown QWs were really thin and really existed. In response to these skeptics, Holonyak and his team at UIUC

employed an “old-fashioned” angle-lapping process (long used in the semiconductor industry to study diffusions). However, in this new more advanced form, Holonyak developed a process for precise  $\sim 1^\circ$  angle-lapping to expose the MQW active regions and then measured the resulting angle-cross section bevel in an SEM to determine the individual layer thicknesses, as shown in Fig. 12.<sup>132,146</sup> These SEM cross section images confirmed that the layer structure was produced as I intended. For a more analytical confirmation, later in 1979, working with a group at Stanford University, we showed by the direct measurement of the interface atomic profiles using Auger electron spectroscopy (AES) combined with sputtering that MOCVD-grown AlGaAs MQW heterostructures were very abrupt and were composed of uniform thin layers as intended as shown in Fig. 13.<sup>147</sup> These heterojunction interface widths were actually better than those for similar computer-controlled MBE-grown superlattices reported in 1974 by Ludeke *et al.* from IBM.<sup>148</sup> Our diode laser angle-lap cross sections and AES results firmly established that MOCVD could produce very precise ultrathin layer structures and that these MQW active regions are of very high structural quality and uniformity. Later, we arranged to have the AlGaAs-GaAs MQW active region of one of our lasers analyzed by TEM to provide

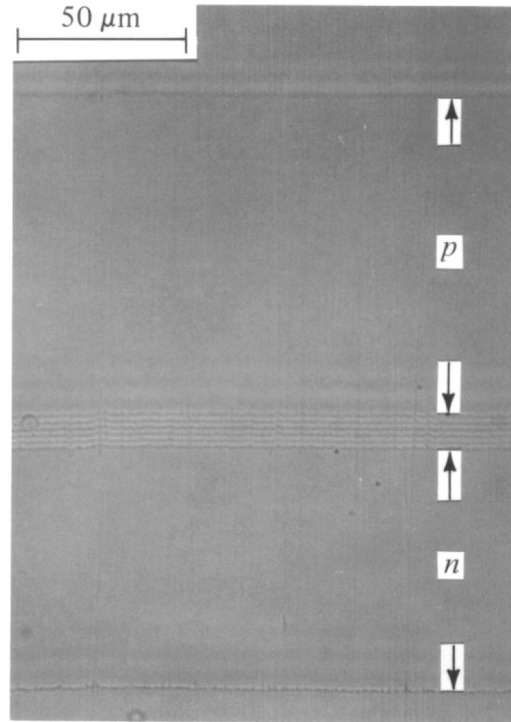


**FIG. 11.** Low-temperature (4.2 K) photoluminescence spectra below and above threshold for an MOCVD-grown AlGaAs-GaAs MQW LD showing distinct LO-phonon-assisted radiative recombination from the quantum states (calculated energies indicated by the rectangular markers 1 and 1' on the wavelength axis). Reproduced from Vojak *et al.*, *J. Appl. Phys.* **50**, 5835 (1979). Copyright 1979, AIP Publishing LLC.

further proof of the MOCVD growth of these ultrathin heterostructures as shown in Fig. 14.

With the demonstration of CW DH and MQW lasers using planar active regions, I began to study the MOCVD growth of LD heterostructures on nonplanar substrates to develop index-guided LDs. In June 1978, I used a GaAs substrate prepared with shallow etched grooves of  $\sim 8 \mu\text{m}$  wide to grow a novel  $\text{Ga}_{0.73}\text{Al}_{0.27}\text{As-GaAs}$  “channel-guide” nonplanar DH laser to improve the lateral optical mode profile.<sup>149</sup> In this structure, the undoped GaAs active region was  $\sim 64 \text{ nm}$  thick (so the laser output did not exhibit quantum-size effects), but it did show very stable single-mode operation CW at 300 K.<sup>150</sup> This work established that MOCVD could grow nonplanar thin active regions, and ultimately, this idea was used to grow nonplanar QW and buried-heterostructure (BH) laser diodes with improved control of the output beam shapes.

Another novel laser structure I developed in 1978 using MOCVD was the “distributed-Bragg-reflector” (DBR) LD.<sup>151,152</sup> This DH structure employed *n*- and *p*-type DBR cladding layers composed of a “dielectric stack” containing 12 to 14 pairs of alternating layers of doped AlGaAs and GaAs on each side of an

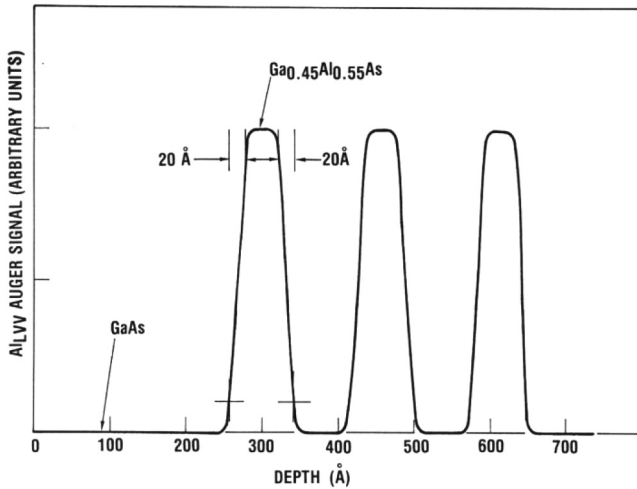


**FIG. 12.** Shallow beveled cross section of a multiple-quantum-well MOCVD AlGaAs-GaAs heterostructure laser diode. The 5+6 Al<sub>x</sub>Ga<sub>1-x</sub>As-GaAs ( $x \sim 0.3$ ) MQW is located between the head-to-head arrows. The polish angle, determined by optical techniques, is  $\sim 0.64^\circ$  and, thus, allows an estimate of the single-layer thickness of  $\sim 120 \text{ \AA}$ . The lower *n*-type Al<sub>x</sub>Ga<sub>1-x</sub>As confining layer ( $x \sim 0.4$ ,  $n_d \sim 10^{18} \text{ cm}^{-2}$ ) and the upper *p*-type Al<sub>x</sub>Ga<sub>1-x</sub>As confining layer ( $x \sim 0.4$ ,  $n_a \sim 5 \times 10^{17} \text{ cm}^{-2}$ ) are measured to be  $\sim 0.8$  and  $\sim 1.1 \mu\text{m}$ , respectively. These dimensions all agree with the calibration of the crystal-growth process. Reproduced from Vojak *et al.*, *J. Appl. Phys.* **50**, 5830 (1979). Copyright 1979, AIP Publishing LLC.

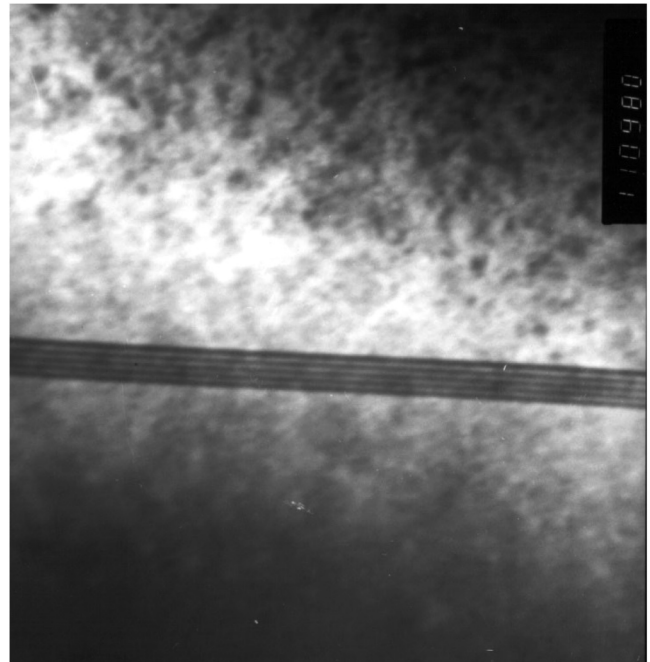
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undoped GaAs active region. In order to obtain low optical losses in these DBR regions, the absorption edge of the GaAs layers in the “mirrors” is “Burstein-shifted” to higher energy due to the high doping concentrations employed in these regions. The DBR period was  $\sim 140 \text{ nm}$  for these LDs. I designed these mirrors using a simple Bragg reflector optical model and an HP Model 6825A Desktop Computer. These lasers operated at 300 K in pulsed mode at  $\sim 1.2 \text{ kA/cm}^2$ . I believe these were the first epitaxial DBRs ever grown by any process. An SEM photograph of the cross section of one of these DBR LDs is shown in Fig. 15. Later, such epitaxial DBR mirrors would become instrumental in the operation of vertical-cavity surface-emitting lasers (VCSELs)—grown of course by MOCVD.

In the Q&A after many of my presentations, one question that was commonly asked was the critical property of MOCVD laser-diode operating lifetime. At Rockwell International, I did not have access to sophisticated laser diode processing, packaging, and testing to answer such questions definitively. However, using a



**FIG. 13.** Auger electron spectroscopy depth profile of an MOCVD-grown  $\text{Al}_{0.55}\text{Ga}_{0.45}\text{As-GaAs}$  MQW laser heterostructure. The interface widths (at the 10% and 90% points) are determined to be  $\leq 2$  nm on each well/barrier combination. Reproduced from Dupuis *et al.*, *Appl. Phys. Lett.* **34**, 335 (1979). Copyright 1979, AIP Publishing LLC.



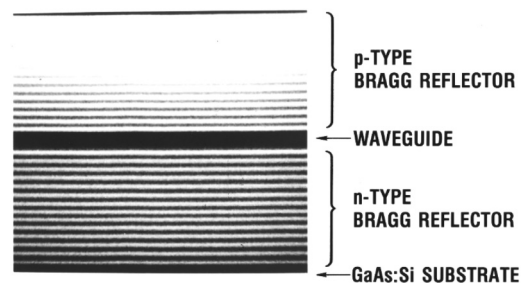
**FIG. 14.** TEM cross section of the QW active region of the same  $\text{AlGaAs-GaAs}$  MQW laser diode as shown in Fig. 12. The darker lines are the GaAs QWs.

simple CW laser diode testing system, I set up one of my LDs (without any facet coatings) for a CW test at “constant current” in my optical lab (not constant power as was commonly used in advanced labs). I had only one stable constant-current power supply and no thermal heat sinks or controlled environment in which to test these devices. The first device I tested employed an  $\text{AlGaAs-GaAs}$  MQW active region that had a cavity length of  $\sim 365 \mu\text{m}$  and an etched low-mesa geometry with an  $8 \mu\text{m}$  wide  $\text{SiO}_2$  *p*-side contact stripe.<sup>153</sup> This first laser operated CW at  $\sim 300$  K (at an uncontrolled room temperature) for over 700 h with very little decrease in the CW output power. I estimated that such devices could easily meet a 1000-h lifetime performance. With the establishment of this basic reliability performance, reported in August 1979, I believed that the question of MOCVD LD lifetime was a question I could definitively respond to in the future. These were also the first published lifetime tests for MQW LDs. A month after my “simple” proof-of-concept of MOCVD LD reliability paper was published, in September 1979, E. J. “Ted” Thrush and James E. A. Whiteaway at Standard Telecommunications Laboratory (STL), Harlow, Essex, UK, reported similar “1000-h” results for MOCVD  $\text{AlGaAs-GaAs}$  LDs.<sup>154</sup> In 1981, Whiteaway and Thrush published another paper clearly proving that MOCVD-grown LDs were as good as or better in initial performance than the best comparable LPE-grown devices made at STL.<sup>155</sup>

Later, when I was employed in the Research Division at Bell Labs beginning in 1979, I built a new more advanced AP-MOCVD reactor for  $\text{AlGaAs-GaAs}$  LDs. In 1983, I worked with Robert L. Hartman and Franklin R. Nash and others in the BTL Murray Hill Area 20 LD Group to determine the useful lifetime of  $\text{AlGaAs}$  QW lasers emitting at  $\sim 850$  nm grown by MOCVD and fabricated using the more advanced processing and testing facilities of

the Area 20 LD Group.<sup>156</sup> The proton-bombarded-narrow-stripe-geometry MOCVD SQW LDs exhibited a degradation rate of  $<1\%/k\text{h}$  or an extrapolated useful lifetime of  $>3.5 \times 10^6$  h at 300 K. This was the first demonstration of the “telecom-quality reliability” of MOCVD LDs. Also in 1983, Duchemin’s group at Thompson CSF reported LP-MOCVD-grown  $\text{InGaAsP-InP}$  DH LDs emitting at  $\sim 1.5 \mu\text{m}$  with 300 K lifetimes  $>10^4$  h without significant degradation.<sup>157</sup> These results further corroborated the practical use of MOCVD for LD production for telecommunication applications and presaged a dramatic

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**FIG. 15.** SEM photograph of the cleaved cross section an  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  distributed-Bragg-confinement (DBC) laser diode structure grown by MOCVD. These are probably the first DBRs grown by MOCVD. The central waveguide layer has a thickness of 286 nm and the Bragg reflectors have a period of 143 nm. Reproduced from R. D. Dupuis and P. D. Dapkus, *Appl. Phys. Lett.* **33**, 68 (1978). Copyright 1978, AIP Publishing LLC.

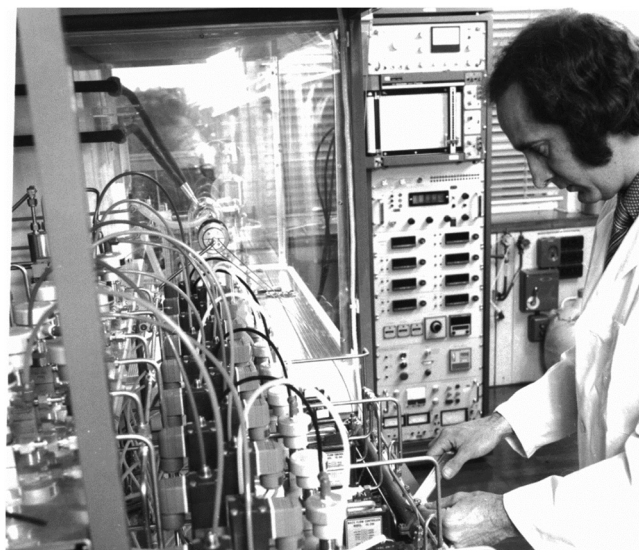
shift in LD production from LPE to MOCVD and clearly proved that MBE technology was not necessary for these applications.

Since the emphasis in the Bell System was shifting to InGaAsP-based LDs emitting at  $\lambda = 1.33$  and  $1.55 \mu\text{m}$  for light sources for advanced telecom systems using low-loss optical fibers, in  $\sim 1984$ – $1985$ , I shifted my research to the MOCVD growth of InP-based materials and devices. However, I had to move my MOCVD lab due to safety concerns, and after this move, I worked on the AP-MOCVD growth of InGaAs/InP heterostructure devices including LDs<sup>158</sup> and the first high-performance InP-based avalanche photodiodes (APDs) grown by MOCVD.<sup>159–161</sup> Of course, now virtually all III–V LDs and avalanche photodetectors, including telecom LDs and APDs, and photonic integrated circuits (PICs) are manufactured using MOCVD.

## V. FURTHER DEVELOPMENT OF THE MOCVD SWISS ARMY KNIFE

### A. MOCVD device advances

After our first MOCVD laser diode papers were published in 1977–1979, and the additional work of many others began to appear, compound semiconductor researchers world-wide began to take a more serious look at MOCVD for the growth of a wide variety of III–V materials and devices. In 1979,  $\sim 18$  months after our first publication of MOCVD LDs, two other groups published demonstrations of AlGaAs–GaAs DH LDs at 300 K grown by MOCVD, one led by E. J. “Ted” Thrush *et al.* at STL. A photograph of Thrush with his home-made MOCVD “kit” is shown in Fig. 16.<sup>162</sup> This system had one-wafer capacity and employed a small “Bass-type” quartz growth chamber with an RF-heated



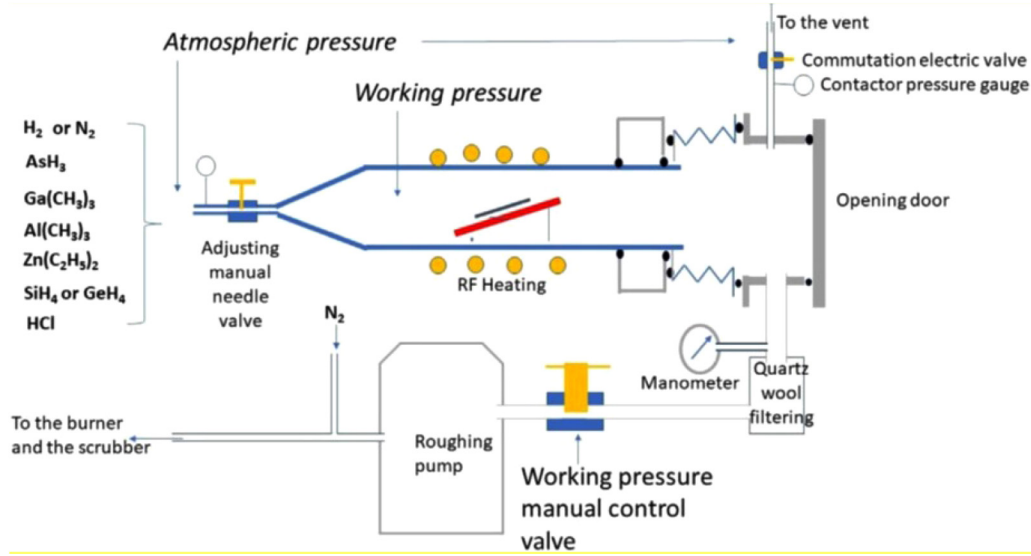
**FIG. 16.** Photograph of E. J. “Ted” Thrush at his AlGaAs–GaAs MOCVD “kit” at STL Harlow in  $\sim 1977$ . This reactor was called “The Mighty Wurlitzer” (a famous musical pipe organ) internally because of all the pipes. Figure provided by E. J. Thrush. Used with the permission of E. J. Thrush.

graphite susceptor. It is clear when you compare Fig. 4 with Fig. 16 that the basic layout of early MOCVD reactors could be very different—Fig. 4 is derived from a chemist’s approach and Fig. 16 is designed by engineers familiar with VPE. The STL MOCVD system also had Tylan FC-260 electronic mass-flow controllers instead of Rotameters and temperature-controlled baths for the MO sources so it was pretty advanced at that time. (STL had a larger budget for the MOCVD equipment than we did at Rockwell.) The other “early” MOCVD AlGaAs–GaAs laser diode was demonstrated by Veenvliet *et al.* at Philips Research Laboratories, Eindhoven.<sup>163–165</sup> As the MOCVD research expanded in both the III–V materials and devices created using this technology, the international III–V community began more serious about the commercial development of MOCVD.

Also in 1979, Duchemin *et al.* at Thompson CSF, Orsay France reported the MOCVD growth of GaAs epitaxial films using subatmospheric reactor pressures of  $\sim 76$  Torr.<sup>166,167</sup> A schematic diagram of this reactor is shown in Fig. 17 and photographs of the system are shown in Fig. 18.<sup>167</sup> Subsequently, they developed this low-pressure MOCVD (LP-MOCVD) for the growth of InP,<sup>168</sup> InGaAs,<sup>169</sup> and InGaAsP<sup>170</sup> and demonstrated the first MOCVD-grown InGaAsP infrared LDs operating at  $1.15 \mu\text{m}$  in 1980.<sup>171</sup> The GaInAsP materials grown by Duchemin *et al.* using LP-MOCVD are probably the first quaternaries grown by MOCVD. Later, in 1983, Duchemin’s team reported the LP-MOCVD growth of low-threshold InGaAsP/InP LDs emitting at  $1.3 \mu\text{m}$ .<sup>172</sup> These LDs had lower threshold current densities than comparable LPE-grown devices, thus establishing MOCVD as a viable technology for long-wavelength telecom LDs. This seminal innovation of subatmospheric-pressure epitaxial growth was derived from Duchemin’s earlier work on low-pressure VPE of Si epitaxial films.<sup>173</sup> Soon, many researchers were exploiting the advantages of low-pressure MOCVD growth, including a thinner “stagnant boundary layer” at the gas–substrate interface, leading to better control of interfaces and doping profiles. With the demonstration of high-performance long-wavelength  $1.33$ – $1.55 \mu\text{m}$  InGaAsP–InP LDs grown by MOCVD, the last nail was in the LPE coffin—it was not needed for the growth of AlGaAs/GaAs or InGaAsP/InP devices. In fact, today the term “MOCVD” almost universally refers specifically to the ubiquitous LP-MOCVD process initially developed by Duchemin and his colleagues at Thompson CSF due to the many advantages that the LP-MOCVD technology offers for large-area uniform growth of complex heterostructure devices.

Many other important innovations were reported for a variety of MOCVD-grown materials. Specifically, important advances for the MOCVD growth of visible-red LEDs and LDs composed of  $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{P}$  quaternary alloys were demonstrated by Japanese workers in the early 1980s. This research was primarily driven by the need for compact and low-cost coherent red light sources for digital-video-disk (DVD) read/write drives. In fact, the first InAlGaP quaternary films were grown by Asahi *et al.* by MBE in 1982,<sup>174</sup> and they also demonstrated the first optically pumped InAlGaP–InGaP DH lasers emitting at  $\sim 630$  nm at 77 K in 1982.<sup>175</sup> Other Japanese workers were using MOCVD to grow this wide-bandgap quaternary. Also in 1982, Suzuki *et al.* at Nippon Electric Corporation (NEC) reported the first MOCVD-grown AlInP–GaInP optically pumped DH lasers emitting at  $\sim 647$  nm at



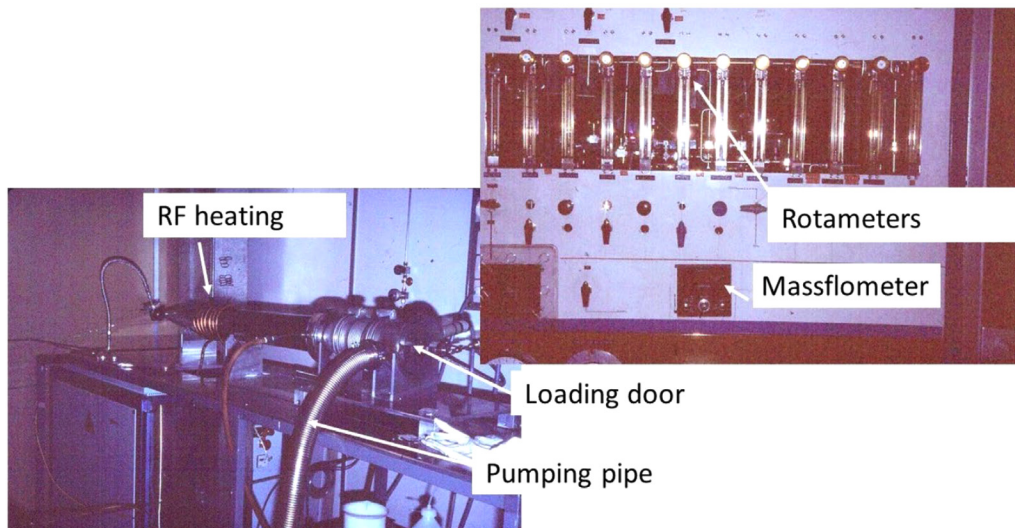


**FIG. 17.** Schematic diagram of the low-pressure MOCVD reactor system used by Duchemin *et al.*, to grow AlGaAs devices (Refs. 166 and 167). Reproduced from J. P. Duchemin, *J. Cryst. Growth*, **601**, 126939 (2023). Copyright 2023, Elsevier.

90 K.<sup>176</sup> In 1983, Hino *et al.*, in the same group at NEC, reported MOCVD-grown InAlGaP quaternary films and LDs operating pulsed at 300 K and emitting at ~683 nm.<sup>177</sup> In 1984, Ikeda *et al.* at Sony reported on AP-MOCVD-grown InAlGaP LDs that operated CW at 77 K and emitted in the red at ~653 nm.<sup>178</sup> In 1985, Ishikawa *et al.* from Toshiba demonstrated CW operation at

-10 °C for MOCVD-grown InAlGaP visible red LDs emitting at ~662 nm.<sup>179</sup> Also in 1985, Ikeda *et al.* at Sony demonstrated 300 K CW operation of red-emitting InAlGaP LDs at ~671 nm.<sup>180</sup> In 1984, Ikeda *et al.* at Sony also reported the low-temperature operation at 77 K of yellow-emitting InAlGaP LDs at ~579 nm.<sup>181</sup> These successes led to the large-scale MOCVD production of red-emitting

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**FIG. 18.** Photographs of the LP-MOCVD reactor used by Duchemin *et al.* for the first low-pressure epitaxial growth of GaAlAs materials (Ref. 167). Note the use of "Rotameters" for the gas flow control and the use of only one mass-flow meter. Reproduced from J. P. Duchemin, *J. Cryst. Growth* **601**, 126939 (2023). Copyright 2023 Elsevier.

LDs for DVD read/write drives and red and high-brightness yellow/orange LEDs for automotive lighting, traffic signals, and information signs throughout the world. In fact, this may have been the first “large-volume” compound semiconductor market addressed exclusively by MOCVD technology.

Another application of MOCVD for the epitaxial growth of compound semiconductors that showed the broad range of applicability and practical importance was the demonstration of the growth of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  films in 1981 by Simon J. C. Irvine and J. Brian Mullin at RSRE, Malvern, UK.<sup>182</sup> This was an important addition to the Swiss Army Knife since later, MOCVD  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  layers grown on sapphire were used to fabricate large-area infrared detectors for many critical scientific and defense applications. For example, such IR detectors were grown by Kenneth Hess of Rockwell International and were installed in the Near Infrared Camera Multi-Object Spectrometer on the Hubble Space Telescope and many other Earth-based astronomy IR telescopes,<sup>183,184</sup> opening up new perspectives on our universe. Additionally, MOCVD-grown  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  detectors were probably installed (although unverified) in the USA’s KH-11 “KENNAN” spy satellites and its derivatives “CRYSTAL” and “KEY HOLE,” increasing the security of many countries.<sup>185</sup>

By the late 1970s, MOCVD research had expanded to such a degree that many researchers felt that an international conference specifically dedicated to the topic should be organized. Thus, the First International Conference on Metal-Organic Vapor Phase Epitaxy” (ICMOVPE-I) was held in Ajaccio, Corsica, France in early May 1981. This conference was organized and strongly supported by the French Ministry of Defense and the French State Secretariat for Research.<sup>186</sup> These organizations had supported the MOCVD research in France and especially the work of Duchemin *et al.* at Thompson CSF in the late 1970s. It is interesting to note that both the first use of the term “l’építaxie” and the first synthesis



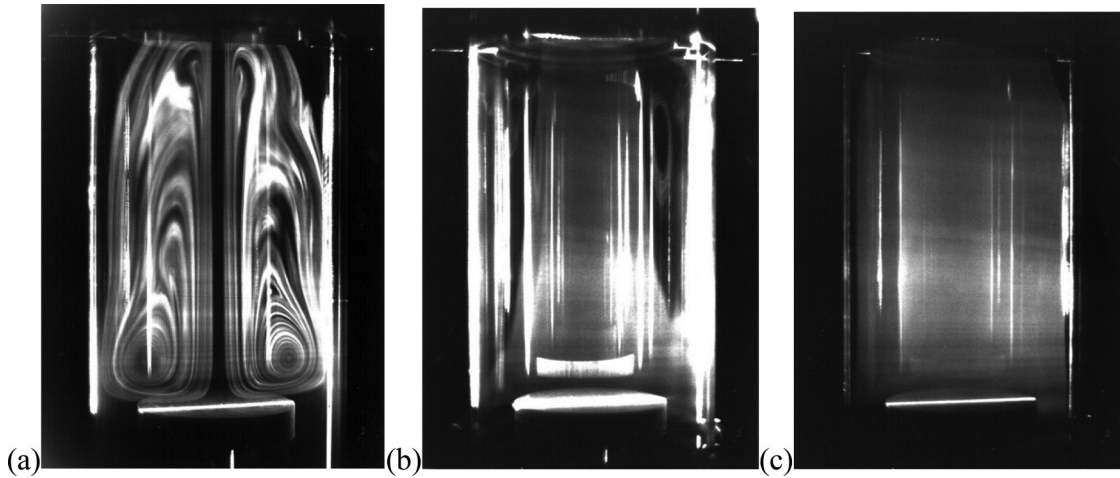
**FIG. 19.** Photograph of the attendees of the ICMOVPE I conference held in Ajaccio, France in May 4–6, 1981 (Ref. 189). Reproduced from *J. Cryst. Growth* 55, p. xi Preface (1981). Copyright 1981, Elsevier.

of an organometallic compound were creations by French researchers. These innovations were perhaps good justifications for the choice of France for the location of ICMOVPE I! At this conference, there were 112 attendees from 13 different countries including France, the USA, the UK, Japan, the Republic of China (Taiwan), Germany, Sweden, and the Netherlands, proving the global scale of interest in the research and development of MOCVD technology. A bonus to the technical presentations, discussions, and excellent food and wine was that we got to see where Napoleon Bonaparte was born!<sup>187</sup> Many of these 112 attendees contributed greatly to the future development of MOCVD after this meeting. A photograph of the attendees of this conference is shown in Fig. 19.<sup>188</sup> The papers presented at this meeting were collected into a special issue of *J. Crystal Growth*, Vol. 55, No. 1 (1981) and the editors, J.-F. Bonfils and J. L. Tetzner, made the statement in the preface “A comparison of the relative merits and drawbacks of this technology with competitive approaches” (referring to MBE and VPE) “shows that presently none of these have decisive advantages and that the versatility of MOVPE may lead shortly to industrial applications.”<sup>189</sup> Actually MOCVD did have decisive advantages that have been widely exploited in commercial use.

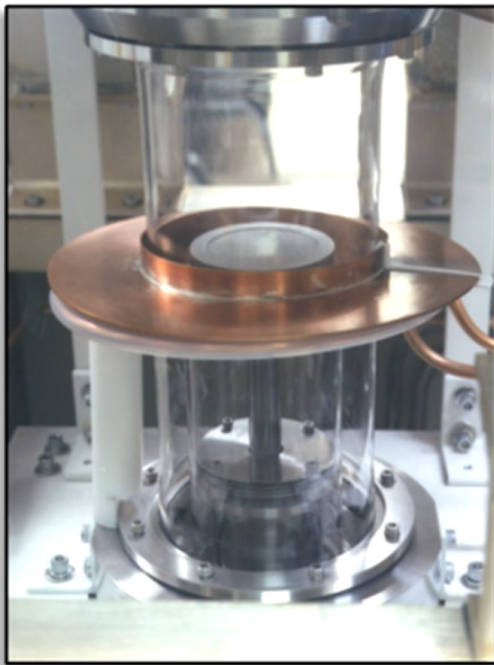
## B. MOCVD reactor development

Other innovations in the 1980s in MOCVD reactor design and growth studies also advanced the State-of-the-Art for layer thickness and alloy composition uniformity, heterojunction interface abruptness, and doping control.<sup>190,191</sup> In the early development of MOCVD, all reactors were “custom built” one-of-a-kind machines or “kits,” each derived from the designer’s experience with Si epitaxy or other III–V epitaxial growth processes—as shown by some of the photographs of the MOCVD reactors in the figures above. One of the first experimental studies that demonstrated the actual flow processes and gas dynamics occurring in an MOCVD reactor was given at the ICMOVPE III Conference in the USA in 1986 by Christine A. Wang *et al.* from MIT Lincoln Laboratory<sup>192</sup> as shown in Fig. 20. These researchers analyzed, modeled, and experimentally studied the operations of a vertical-geometry rotating-disk “stagnation-point-flow” atmospheric-pressure reactor shown in Fig. 21 that they subsequently used for highly uniform AlGaAs QW LD growth.<sup>193–196</sup> They showed that using analytical models of the growth process and environment combined with experimental studies, they could design extremely uniform MOCVD reactors with very abrupt heterojunction interfaces.<sup>197</sup>

Another important development for the advancement of the capabilities of the MOCVD Swiss Army Knife was the use of advanced gas-phase chemical kinetics, surface kinetics, and hydrodynamics computer models that can provide for solutions to the multifaceted boundary conditions occurring in an MOCVD system. Important contributions to understanding the MOCVD processes were made by Klavs F. Jensen and his group at the University of Minnesota.<sup>198</sup> Additional seminal contributions in modeling the chemical kinetics and hydrodynamics in MOCVD growth were made by Mike Coltrin and a team of workers at Sandia National Laboratories using their prior experience in the



**FIG. 20.** Flow patterns for various configurations of a MOCVD vertical stagnation-point-flow reactor using  $\text{TiO}_2$  particles and laser visualization. Image (a) is for a coaxial pipe injector; (b) is for a “porous plug” shower-head reactor with a 3.8 cm diameter injector; (c) is the same as (b) but with a 7.6 cm diameter injector—approximately the cross section of the chamber. The reactor chamber in (c) is operating in nearly ideal laminar flow conditions. Reproduced from Wang *et al.* (Ref. 192), *J. Cryst. Growth* **77**, 136 (1986). Copyright 1986, Elsevier. Further discussion can be found in Refs. 190 and 191.

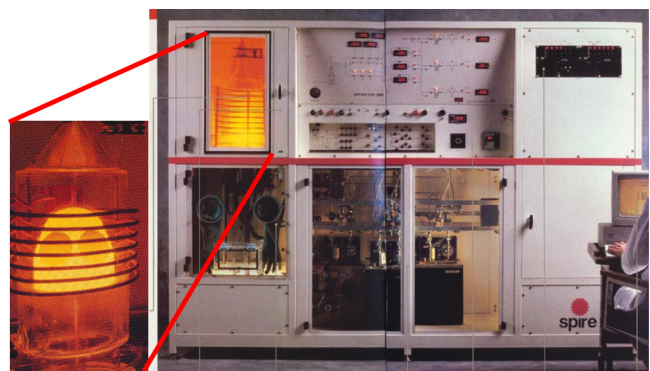


**FIG. 21.** Photograph of the growth chamber of the RF-heated stagnation-point-flow MOCVD reactor designed by Wang *et al.* that was developed from their flow visualization studies (Ref. 190). This reactor produced very uniform AlGaAs-GaAs MQW LDs on 2 in. diameter substrates (Refs. 193 and 194). Reproduced from C. A. Wang (Ref. 190), *J. Cryst. Growth* **506**, 190 (2019). Copyright 2019, Elsevier.

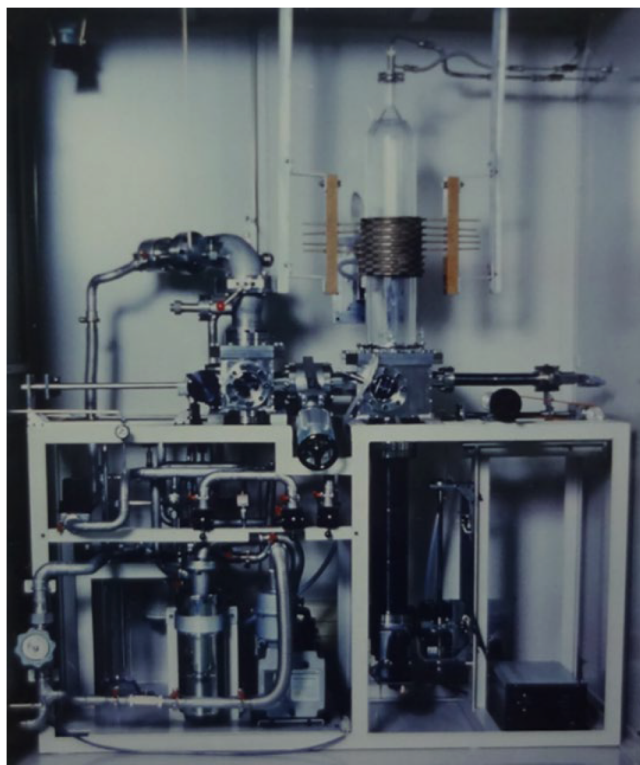
modeling of Si-based VPE reactors.<sup>199,200</sup> The Sandia CVD Sciences Group provided tools for the detailed analysis of MOCVD systems, and this work contributed greatly to the practical design and understanding of the large-area commercial MOCVD reactors in common use today.

In the middle 1980s, “standardized” commercial MOCVD reactors became available from a few companies. For example, in 1984, Spire Corporation in the USA offered the SPI-MO 450 MOCVD reactor, as shown in Fig. 22, which was a “barrel-type” CVD system, similar to those used for HVPE of GaAsP, having a capacity for five 2.0 in. diameter wafers per run that could operate at atmospheric or

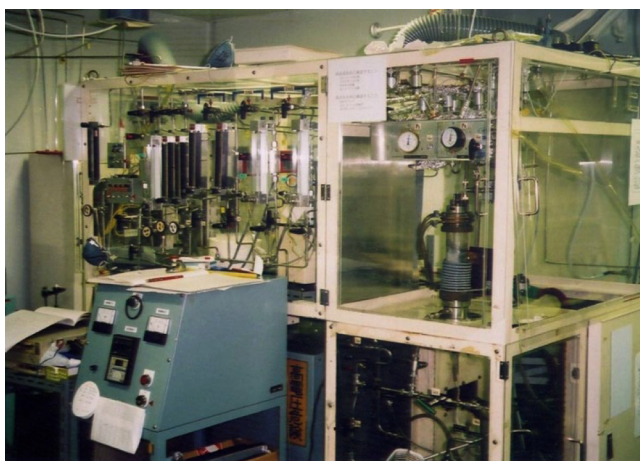
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**FIG. 22.** Photograph of the growth chamber of the Spire Corp. SPI-MO 450 multiwafer MOCVD reactor of the type sold in 1984. The view of the growth chamber during epitaxy is shown in the photograph on the left. Reproduced from the Spire Corp. SPI-MO 450 equipment brochure.



**FIG. 23.** Photograph of a Taiyo Nippon Sanso VR2000 MOCVD reactor from 1983. Photograph courtesy of Taiyo Nippon Sanso Corporation. Used with permission of Mayank Bulsara.



**FIG. 24.** Photograph taken in 1984 of the "home-made" MOCVD reactor fabricated by H. Amano and Y. Koide at Nagoya University. Note the use of Rotameters for gas flow control. Compliments of Professor Hiroshi Amano. Photograph taken by Professor Kazumasa Hiramatsu. Used with permission of Professor Hiramatsu (Ref. 204).

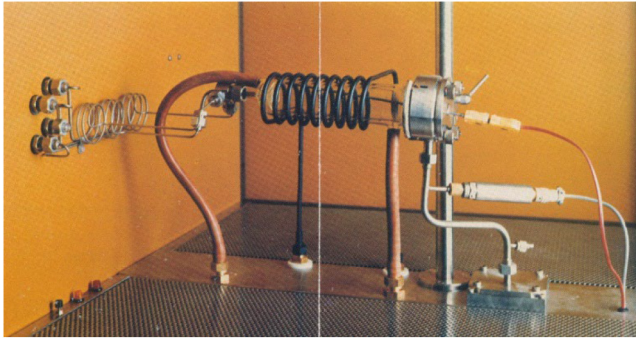
low pressure.<sup>201</sup> In 1985, Spire announced the larger SPI-MO 1000 MOCVD reactor with a capacity for twenty 2.0 in. diameter wafers. In 1986, Spire offered the smaller "research-scale" SPI-MO 240 MOCVD reactor with a capacity for two 2.0 in. diameter wafers. Because of the fundamental design of the growth chamber used in these Spire systems, the layer uniformity was not particularly good.

In Japan, Taiyo Nippon Sanso developed the HR2000 horizontal-flow MOCVD reactor with a capacity of one 2.0 in. diameter wafer in 1983 and started commercial sales in 1985 of the HR3000 2 in. × 1 and the HR4000 2 in. × 3 reactors.<sup>202</sup> A photograph of a Taiyo Nippon Sanso VR2000 reactor from 1983 is shown in Fig. 23. Also in early 1980s, ULVAC in Japan created a single-wafer MOCVD reactor for Isamu Akasaki at Nagoya University for GaN growth.<sup>203</sup> This was the reactor that Hiroshi Amano used to grow the first *p*-type GaN:Mg films and other III-N MOCVD research work. The earlier "home-made" III-N MOCVD reactor was built in Akasaki's lab by Amano and Dr. Yasuo Koide and was used to develop low-temperature AlN/sapphire buffer layer technology as shown in Fig. 24. A photograph of Amano working on this reactor is shown in Fig. 25.



**FIG. 25.** Photograph of Hiroshi Amano working on the "home-made" III-N "MOCVD reactor in the Nagoya University MOCVD cleanroom in 1984. Compliments of Professor Hiroshi Amano. Photograph taken by Professor Kazumasa Hiramatsu. Used with permission of Professor Hiramatsu (Ref. 204).

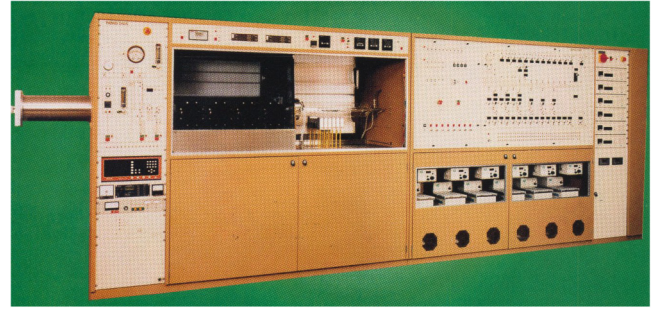
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**FIG. 26.** Photograph of the RF-heated quartz reactor chamber of the Metals Research MR 100AS MOCVD reactor. This reactor employed the famous “Bass cell” growth chamber design. Reproduced from the MR MOCVD 100AS reactor brochure (Ref. 205).

As noted above, some of these early small-research-scale commercial reactor chamber designs available from UK manufacturers were derived from the horizontal quartz chamber with RF heating designed by Sydney Bass in his early work—commonly referred to as “The Bass Cell.”<sup>103</sup> An example is the Cambridge Instruments/ Metals Research MR 100AS MOCVD reactor with one 2.0 in. diameter wafer capacity offered in 1984 and shown in Fig. 26. Similar horizontal-chamber MOCVD reactors were developed by English Electric Valve and Thomas Swan Scientific Equipment Company, Ltd. (TSSEL). A photograph of an early TSSEL MOCVD reactor is shown in Fig. 27. The schematic drawing of a TSSEL standard 2.0 in. diameter “Epitor” “Bass Cell”-type MOCVD reactor chamber is shown in Fig. 28.<sup>205</sup>

Later, in about 1988, Rajaram Bhat, then at Bellcore in Red Bank, NJ, ordered an MOCVD reactor from TSSEL with a chamber that he had custom-designed that employed some of the concepts developed in ~1986 by Wang *et al.*<sup>192</sup> Bhat licensed the Wang patent and worked with Swan engineers to custom-design and build a new reactor using the vertical stagnation-point design.<sup>206</sup> The first TSSEL MOCVD reactor manufactured for Bhat had a single 2.0 in. diameter wafer capacity and a quartz-chamber and a rather simple “fine mesh” gas injection system made according to Bhat’s modification of Wang’s design—but it was not a close-coupled showerhead (CCS) design since the susceptor was several inches from the showerhead. In ~1994, working with John Crawley at TSSEL, Bhat improved on the design of the showerhead of his vertical-geometry MOCVD reactor, and this reactor chamber design moved the showerhead close to the susceptor, employing some of the prior innovations of Wang *et al.*<sup>192,193,195</sup> and more recent work on CCS reactors by David W. Weyburne and Brian S. Ahern who were at the USAF Rome Laboratory, Hanscom AFB, MA.<sup>207,208</sup> In response to this order, Thomas Swan began the commercial development of the basics of the “close-coupled showerhead—CCS” MOCVD research-scale reactors (currently sold by AIXTRON). The novel ideas Bhat incorporated into the design of the injection “showerhead” in his revised “second-generation” Thomas Swan reactor (the first “truly CCS” commercial MOCVD



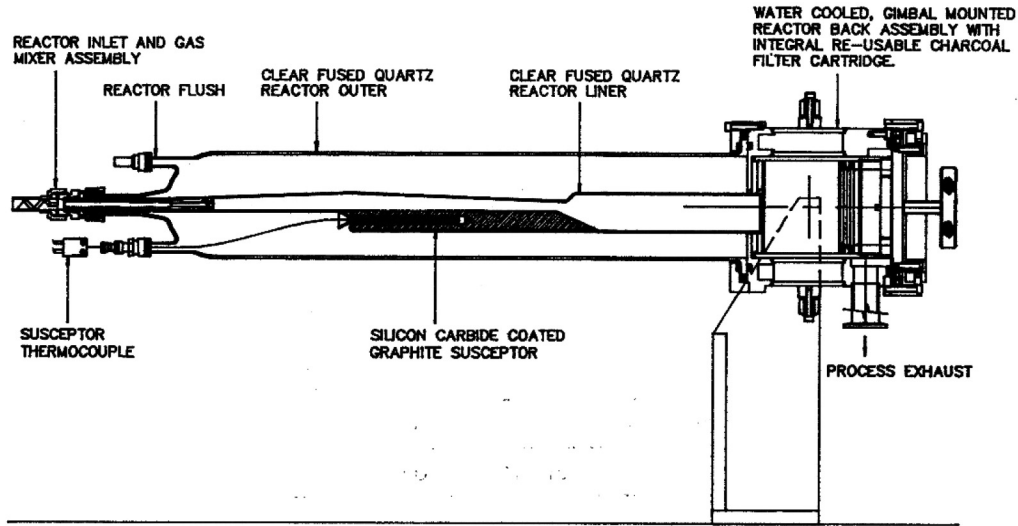
**FIG. 27.** Photograph of an early TSSEL LP-MOCVD reactor system with a quartz horizontal reactor chamber and six MO source baths. Note that this system has a load-lock for loading wafers into the reactor and an Inficon mass spectrometer controller mounted in the left side of the system cabinet. Photograph from TSSEL reactor sales brochure.

reactor) derived from the porous “fused-quartz frit” gas injection element used in the “vapor-levitation epitaxy” innovation for III–V chloride VPE reactors invented for the growth of As- and P-containing epitaxial films by Herbert Cox *et al.* who was also working at Bellcore.<sup>209,210</sup> In 1996, the first of the early TSSEL CCS all-stainless steel reactors with a two 2.0 in. diameter wafer capacity was delivered to the University of Ghent for the growth of GaN films.<sup>211,212</sup>

Independently, beginning in 1987, Ahern and Weyburne at the USAF Rome Laboratory, developed the CCS concept using their patented chamber designs<sup>213</sup> and in ~1993 worked with Spire Corp. in nearby Bedford MA to build an all-stainless-steel CCS MOCVD reactor based upon this patent. This CCS MOCVD reactor had a 4.0 in. diameter wafer capacity and a water-cooled close-coupled “showerhead” gas injection system derived from Ahern and Weyburne’s patent and subsequent research<sup>214</sup> and employed a somewhat different design than the Bhat/Thomas Swan system. Using this reactor, they demonstrated the uniform growth of InP, InGaAs, InGaP, GaAs, and AlGaAs on a single 4.0 in. diameter substrate in 1994.<sup>208,214</sup> In 1997, Spire Corp. offered for sale the Model 400S MOCVD system based on the CCS Weyburne designs shown in Fig. 29.<sup>214</sup>

Another middle-1980s supplier of commercial MOCVD reactors was AIXTRON, founded in Aachen, Germany in 1983. The first AIXTRON reactor had a 1 × 2.0 in. wafer capacity and was marketed as the AIXTRON-200 series, which was later upgraded to one 4 in. wafer or 3 × 2 in. wafer capacity.<sup>215,216</sup> The first commercial version of the AIXTRON-200 system was sold to AEG Research Center in Ulm, Germany, in ~1984.<sup>217,218</sup> In 1987, AIXTRON co-founder Holger Jürgensen and his colleague Meino Heyen filed a German patent for the invention of an improved horizontal-tube MOCVD reactor chamber, which followed a design originally developed at RWTH in Aachen.<sup>219,220</sup> A photograph of Jürgensen at the controls of an early AIXTRON MOCVD reactor is shown in Fig. 30.<sup>215</sup> This patent describes a reactor chamber having a horizontal round outer tube and an inner rectangular liner tube and employed a susceptor heated with a lamp and had an

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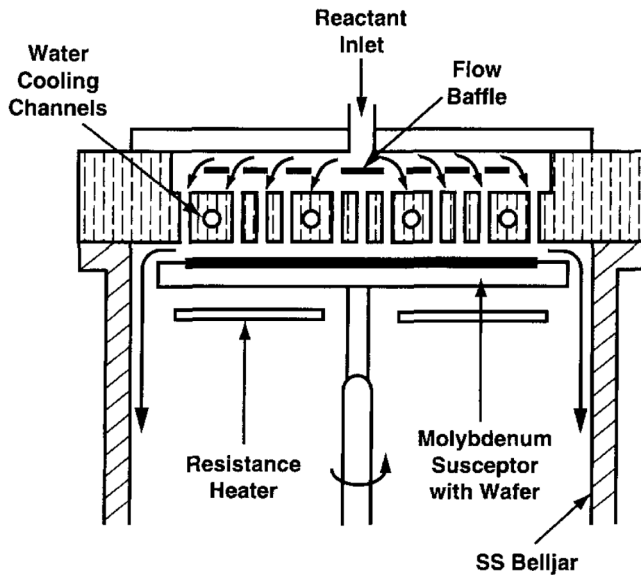


**FIG. 28.** Schematic cross-sectional diagram of a TSEL Epitaxial quartz reactor chamber modeled after the “Bass Cell.” This system had a capacity for one 2 in. diameter wafer (Ref. 205). Reproduced from TSEL reactor sales brochure.

improved uniformity. This basic MOCVD reactor chamber design was modified many times to increase the substrate area, uniformity, and growth efficiency of the AIXTRON horizontal reactors. A photograph of an AIXTRON AIX 202 RD LP-MOCVD reactor with a

horizontal quartz chamber, lamp heating, and a capacity for two 2.0 in. diameter wafer is shown in Fig. 31. However, AIXTRON made a dramatic switch in the early 1990s for the design of their production-scale MOCVD systems with the licensing of an innovative new MOCVD “horizontal-style” chamber reactor configuration to be described next.

In 1988, Peter Frijlink at the Laboratoires d’Electronique et de Physique Appliquée (LEP) in Limeil-Brévannes, France reported (and patented in 1989) the design and operation of a novel “planetary” multiwafer MOCVD reactor that was basically a horizontal-flow geometry design but employed susceptor rotation combined

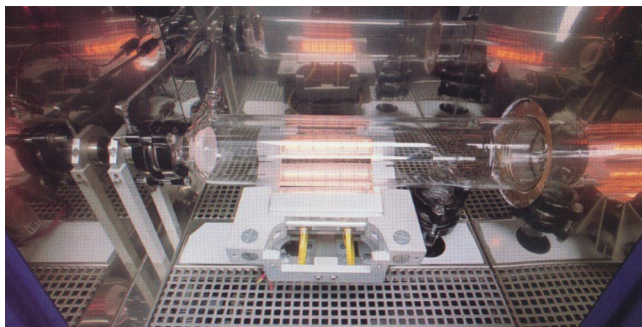


**FIG. 29.** Schematic diagram of the Weyburne *et al.* close-coupled showerhead MOCVD reactor chamber. This design is similar to the one commercialized in the Spire Model 400S reactor system in 1997 (Ref. 214). Reproduced from D. W. Weyburne and B. S. Ahern (Ref. 214), *J. Cryst. Growth* **170**, 77 (1997). Copyright 1997, Elsevier.



**FIG. 30.** Photograph of Holger Jürgensen, co-founder of AIXTRON, at the controls of an early AIXTRON prototype horizontal MOCVD reactor then located at RWTH Aachen University. Photograph courtesy of M. Heuken. Used with permission of M. Heuken.

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**FIG. 31.** Photograph of the chamber area of an AIXTRON AIX 202 RD LP-MOCVD reactor with a horizontal quartz chamber, lamp heating, and a capacity for two 2.0 in. diameter wafers (Ref. 221). Reproduced from AIXTRON AIX 202 RD MOCVD reactor sales brochure.

with individual wafer counter rotation using a “gas-foil” levitation mechanism to improve the uniformity of a standard “horizontal” epitaxial growth system.<sup>222–224</sup> Frijlink modeled the reactor performance in detail and used it to demonstrate a variety of excellent uniformity AlGaAs-GaAs heterostructure devices. This innovative reactor was able to produce extremely uniform epitaxial layers on seven 2.0 in. diameter wafers or five 3.0 in. diameter wafers in a single run. The patent for this reactor design innovation was subsequently licensed and then further developed by AIXTRON to create their first generation of planetary-geometry LP-MOCVD commercial reactors, the AIX 2000 series, beginning in the late 1980s/early 1990s. Figures from the Frijlink patents are shown: Fig. 32(a) showing the gas injection design and planetary chamber cross section designed for five wafers and Fig. 32(b) showing the arrangement of the distributed exhaust ports inside the chamber.

Another commercial MOCVD reactor system based on a different technology was developed in the middle 1980s by EMCORE in the USA.<sup>225,226</sup> EMCORE was founded in 1984 by Norman E. Schumaker, Richard A. Stall, and William R. Wagner, all of whom were working at that time in the Bell Labs Murray Hill Laser Diode Development Group—referred to internally as the “Area 20 LD Group.” This Bell Labs group, led by Schumaker, had the responsibility to develop and produce high-reliability AlGaAs-GaAs DH IR lasers for the first-generation fiber-optic telecommunications systems that Bell System’s telecom operating companies required. At first, following the LPE AlGaAs-GaAs DH LD work done beginning in 1971 by Morton B. Panish and Izuo Hayashi<sup>227</sup> in the Bell Labs Physics Research Division (called “Area 10”), they worked on developing the production of LPE LDs but found that device yields were very low. Later, they turned to also develop MBE growth, following Al Cho’s AlGaAs MBE-LD work done beginning in 1974<sup>78</sup> that had been performed also in the Research Division’s Area 10. The Area 20 LD Group was not successful in the MBE LD development effort, however, because their “home-made” MBE system was not very vacuum tight with a minimum load-lock pressure only as low as  $\sim 10^{-5}$  Torr and their expensive specially designed commercial MBE LD production system that they had purchased from Physical Electronics (PHI) Inc. (a maker of surface-science analysis tools in

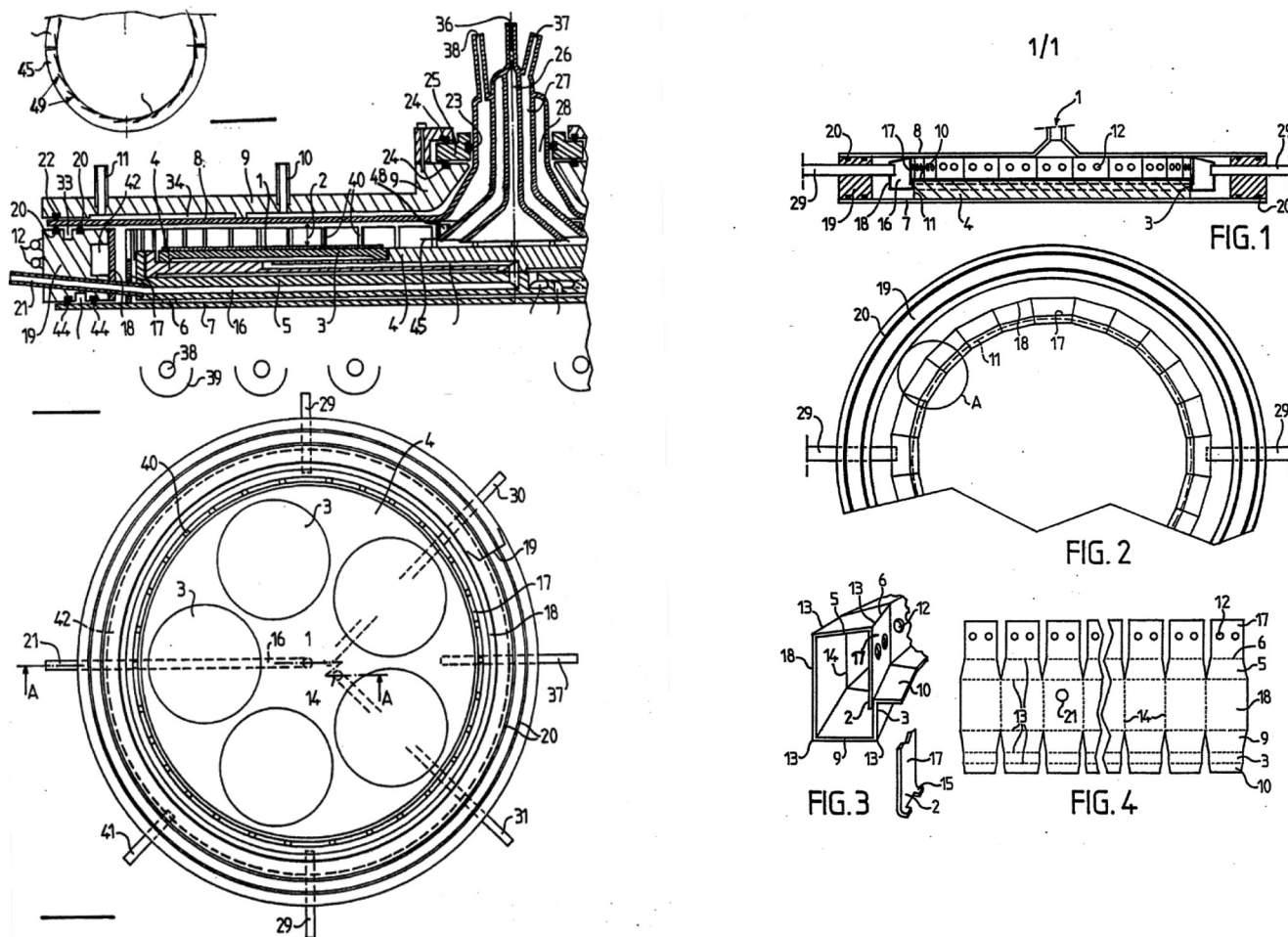
Minnesota) never worked well because the vacuum flanges tended to leak when the cryopanel was cooled with  $\text{LN}_2$ , leading to poor morphology for AlGaAs layers.<sup>228,229</sup> The Bell Labs Area 20 MBE AlGaAs LD production plans ended by about 1984.

However, sometime after my MOCVD LD papers were published in 1977–1978, Schumaker and his team started to also consider developing MOCVD for LD production in a third parallel effort. Consequently, when in 1979, at the invitation of Mort Panish, I joined his group in the Bell Labs Physics Research Division in Area 10, I found that the Area 20 LD Group had a large team working on the design and building of an “automated” production-scale MOCVD reactor for AlGaAs-GaAs LD development.<sup>230</sup> Unfortunately, I had a two-year delay in getting my Bell Labs cleanroom lab space renovated before I could start building (by myself) my new improved MOCVD reactor that I designed so I started MOCVD growth of AlGaAs-GaAs LDs at Bell Labs again in 1981. Working in collaboration with Robert L. Hartman and Franklin Nash from the Area 20 LD device team, we demonstrated reliable “telecom quality” MOCVD AlGaAs-GaAs QW LDs at Bell Labs in 1983.<sup>156</sup>

Using the MOCVD reactor design knowledge that they had developed in Area 20, Schumaker, Stall, and Wagner left Bell Labs in 1984 and founded the Electronic Materials Corporation (EMCOR—without an “E” at the end) to build MOCVD reactors commercially.<sup>231,232</sup> After studying various MOCVD reactor geometries the early days after founding EMCORE, they eventually exploited the vertical-flow rotating-disk reactor with a high-speed rotation stagnation-point-flow chamber design demonstrated in 1986 by Wang *et al.*,<sup>193,195</sup> combined with the low-pressure growth approach employed by Duchemin<sup>166,167</sup> for their commercial “Turbo-Disc” LP-MOCVD reactors that employed a “Flow-Flange” gas injection system.<sup>190,192,233</sup> While the first EMCORE MOCVD reactor employed a quartz chamber, subsequent systems used an all-stainless-steel design. The first of these systems was a dual-chamber reactor (locally referred to as the “EMCORE DFM”) that was installed in the University of Illinois at Urbana-Champaign Microelectronics Research Center in Urbana, IL, in  $\sim 1988$ .<sup>234</sup> The EMCORE MOCVD reactor technology was subsequently sold in 2003 to VEECO in the USA and is still marketed under the “TurboDisc®” name.<sup>235</sup>

### C. Commercial development of MOCVD sources

In addition to the development of standardized commercial MOCVD reactors, another important development in the establishment of MOCVD as the “Swiss Army Knife” for III–V devices was the improvement of the purity of commercially available MO and hydride sources. As noted above, there were early efforts to use “industrial-grade” MO sources and later, “electronic-grade” small-batch sources with basically uncontrolled and unanalyzed properties. In some cases, specially purified MO sources were made by groups exploring MOCVD.<sup>96,236</sup> As an example of the efficacy of this approach, in 1982, Kenneth L. Hess, a physical organic chemist, and his colleagues at Rockwell purified TMGa using a novel all-quartz high-purity fractional distillation column specially designed and built for this purpose. Using this purified TMGa, they achieved a marked improvement in the electron mobility of



**FIG. 32.** Schematic diagrams of the planetary MOCVD reactor chamber patented by Frijlink in French patent 2,628,984 filed on March 22, 1988 and 2,638,020 filed on October 14, 1988. Figure (a) shows the injection system and the planetary wafer rotation. Figure (b) shows the diagram of the annular exhaust system.<sup>223</sup> These concepts were improved and commercialized by AIXTRON in their Planetary Series of reactors. Reproduced from P. M. Frijlink, French patent FR2628984A1 (Ref. 223) and P. M. Frijlink, French patent FR2,638,020A1 (Ref. 224).

the as-grown undoped GaAs films for both AP-MOCVD and LP-MOCVD growth conditions.<sup>236</sup> For LP-MOCVD grown GaAs films of  $\sim 20 \mu\text{m}$  thick, the 77 K mobility increased from  $\mu_n = 65\,000 \text{ cm}^2/\text{V s}$  for layers grown with “as delivered” TMGa to a maximum of  $\mu_n \sim 106\,000 \text{ cm}^2/\text{V s}$  for GaAs films grown with the repurified TMGa. With repurified TMGa and with the use of purified  $\text{AsH}_3$ , the 77 K net carrier concentration was reduced to  $N_D - N_A = 4.8 \times 10^{13} \text{ cm}^{-3}$  and 77 K mobility increased to  $\mu_n \sim 125\,000 \text{ cm}^2/\text{V s}$ .<sup>236</sup> These values are comparable to the high-purity GaAs grown by Seki in 1975 using purified TEGa<sup>69</sup> and showed that TMGa could also be used for the growth of high-mobility GaAs films.

As the market for these chemicals increased, more resources were developed to understand the optimal synthesis routes and

purification processes for the large-scale cost-effective commercial production of the primary high-purity metal alkyls.<sup>237,238</sup> An especially important development in this area was the invention in  $\sim 1983$  of the “adduct-purification technique” for metalorganics developed by the chemist Anthony Jones at the University of Liverpool.<sup>239,240</sup> This process was subsequently commercialized by Epichem Ltd.,<sup>241</sup> founded by Barry Leese *et al.* near Liverpool, in Bromborough, Merseyside, UK, and was especially important for the purification of trimethylindium,  $(\text{CH}_3)_3\text{In}$ , for the growth of InP and related materials.<sup>242</sup> Several other vendors of MO sources developed other proprietary approaches to high-purity precursor production.

Another important but little remembered event in the development of metalorganic sources occurred in 1983—Carol R. Lewis *et al.*



at Varian Associates in Palo Alto, CA, published the first Mg doping in MOCVD using the precursor bis(cyclopentadienyl magnesium)— $\text{Cp}_2\text{Mg}$ —as a source of Mg acceptor doping in GaAs films.<sup>243</sup> Until this time, virtually all *p*-type doping in MOCVD III–V growth employed diethylzinc (DEZn) for Zn acceptor doping. However, Zn has a fairly high diffusion coefficient in many III–V semiconductors. Lewis *et al.* used  $\text{Cp}_2\text{Mg}$  that they had purified using distillation and they were able to get a source pure enough to succeed in making *p*-type GaAs films with *p*-type doping with 300 K free-hole concentrations over four orders of magnitude from  $p = 10^{15} \text{ cm}^{-3}$  to  $10^{19} \text{ cm}^{-3}$  (as determined from Hall-effect measurements) with very little acceptor compensation. This work sets the stage for Akasaki and Amano to develop the effective *p*-type Mg doping in GaN in 1989,<sup>244</sup> an important innovation since the Zn acceptor states are so far from the valence band in GaN.

#### D. MOCVD *in situ* growth monitoring

Many other important developments in MOCVD materials were made in the 1990s and 2000s that greatly expanded the variety and improved the quality and yield of devices created by this process—sharpening and adding “blades” to the MOCVD Swiss Army Knife, e.g., the development in ~1992 of the Thomas Swan “EPISON” *in situ* monitors for the direct real-time measurement and control of the metalorganic source molar flow rates.<sup>245</sup> Another important innovation was the development of systems in ~1991 for *in situ* optical monitoring of the wafer surface using reflectance-anisotropy spectroscopy (RAS) or reflectance-difference spectroscopy (RDS) that provides real-time information on the details of the MOCVD growth process. RAS was pioneered for MOCVD *in situ* monitoring in ~1991 by Wolfgang Richter’s group at the Technical University of Berlin.<sup>246,247</sup> Thomas Zettler, working in Richter’s group, created a slogan for this study: “*Light is a gentle tool!*” and they developed this tool to study the epitaxial growth surfaces and interfaces *in situ* during an actual growth run with high spatial and temporal sensitivity.

A similar process to RAS, RDS, was originally developed by David Aspnes at Bellcore,<sup>248</sup> and it was applied to MOCVD by Edward Colas *et al.* at Bellcore also in 1991.<sup>249</sup> The commercial development of such tools, for example, those pioneered by LayTec GmbH, founded in 1999 in Berlin Germany by Zettler, Kolja Haberland, and Markus Weyers, became an important application of this technology for effective and efficient commercial epitaxial materials production.<sup>250,251</sup> LayTec delivered its first EpiRAS system to Hilde Hardtdegen at Research Center Jülich in Germany in 1998—even before the LayTec company was officially formed.<sup>251</sup>

*In situ* optical monitoring and control of the growth of AlGaAs layers in an AP-MOCVD reactor using laser reflectometry with a He-Ne laser was reported in 1991 by Sankur *et al.* at the Rockwell International Science Center in Thousand Oaks, CA.<sup>252</sup> This group demonstrated for the first time real-time closed-loop control of the thickness and alloy composition of the growth of AlGaAs layers—including graded-alloy-composition  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  films.

Thus, by the early 2000s, all of the major technological pieces were in place to support the large-scale commercial exploitation of the MOCVD Swiss Army Knife’s wide range of capabilities for the production of a large variety of compound semiconductor devices.

#### VI. REST OF THE STORY OF THE MOCVD SWISS ARMY KNIFE

It is beyond the scope of this paper to discuss many important contributions to the science and technology of MOCVD in any detail or even to mention many of the most important past works let alone describe the vast quantity of the most recent work performed in the 2000s that highlight the power and flexibility of the MOCVD Swiss Army Knife. Such additional areas of research and development include the MOCVD growth and further development of InAlAs-InGaAs IR quantum-cascade lasers,<sup>253,254</sup> the growth of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  materials for far-IR detectors,<sup>255</sup> III–V nanostructures of many kinds,<sup>256,257</sup> III–Vs on Si,<sup>258–263</sup> vertical-cavity surface-emitting lasers (VCSELs),<sup>264</sup> III–N UV LEDs<sup>265,266</sup> and III–N LDs,<sup>267</sup> III–N electronic devices,<sup>268</sup> and advanced integrated photonic devices, e.g., photonic integrated circuits for high-speed telecommunications.<sup>269</sup> Among the most recognized and seminal of the “more or less recent” advances since the middle 1980s in the MOCVD field are those related to the MOCVD growth of the wide-bandgap III–N materials on sapphire substrates, pioneered in 1971 by Manasevit *et al.*<sup>63</sup> In fact, the volume production of III–N devices, e.g., LEDs, LDs, HEMTs, etc., has been primarily responsible for the current high economic and “societal value” of MOCVD. Some of these important innovations related to III–Ns are listed below in Table I.

For more information on the fundamentals, including the hydrodynamics, kinetics, and chemistry of the MOCVD process, the reader is referred to the books by G. B. Stringfellow<sup>277,278</sup> and the many overviews of MOCVD process technology, e.g., R. M. Biefeld *et al.*<sup>279</sup> and an overview of CVD by A. C. Jones.<sup>280</sup> The extensive literature on MOCVD is constantly expanding, but one good source for a collection of recent work is the Proceedings of the International Conference on Metalorganic Vapor Phase Epitaxy held every two years since 1984 (the first one, ICMOVPE I, was held in France in 1981 as noted above). These are published by North-Holland/Elsevier Science Publishers.

#### VII. FUTURE DEVELOPMENT OF THE MOCVD SWISS ARMY KNIFE

It is hard to give any accurate picture of the future of MOCVD except to say that it will continue to impact the lives of almost all of the people on Earth (and the Moon and maybe Mars) and, hopefully, will continue to contribute to the sustainability of our societies on Earth and the knowledge and understanding of our universe. It is clear that the experimental introduction of the MOCVD process by Manasevit in 1967–1968 is one of the great technical contributions made in the 20th century to improve our current way of living. We can expect that improved and more efficient metalorganic source production and larger and more efficient reactors will be developed. Artificial Intelligence and Machine Learning will soon play a role in real-time reactor controls, and the use of *in situ* sensors and real-time monitoring with feedback control will be expanded. The development of virtual/augmented reality displays, autonomous vehicles, implanted biosensors, flexible electronics, and geostationary and low-earth-orbit satellites, e.g., the Space X Starlink system, for world-wide communications and sensing, are new and rapidly expanding applications that will

**TABLE I.** Some III-N-related MOCVD advances.

Year	Authors	Affiliation	Result
1986	H. Amano and I. Akasaki	Nagoya Univ.	High-quality GaN on (0001) sapphire by MOCVD <sup>270</sup>
1989	H. Amano and I. Akasaki	Nagoya Univ.	Demonstrated effective <i>p</i> -type doping of MOCVD-grown GaN using Mg dopants that were activated by low-energy electron-beam irradiation (LEEBI). <sup>244</sup>
1990	H. Amano and I. Akasaki	Nagoya Univ.	Demonstrated an optically pumped GaN laser grown by MOCVD on sapphire at 300 K. <sup>271</sup>
1991	S. Nakamura <i>et al.</i>	Nichia	Demonstrated <i>p</i> -type doping in MOCVD GaN:Mg using thermal activation of the Mg acceptors. <sup>272,273</sup>
1991	S. Nakamura <i>et al.</i>	Nichia	Demonstrated high-efficiency and high-power blue InGaN LEDs on sapphire by MOCVD. <sup>274</sup>
1992	M. A. Khan <i>et al.</i>	APA Optics	Reported the first AlGaIn-GaN two-dimensional electron gas grown by MOCVD. <sup>268</sup>
1993	Watanabe <i>et al.</i>	Nagoya Univ.	Demonstrated GaN on Si using AlN buffer layer. <sup>263</sup>
1996	S. Nakamura <i>et al.</i>	Nichia	Demonstrated the first InGaIn-GaN MQW LDs grown by MOCVD. <sup>274</sup>
2019	M. Kushimoto <i>et al.</i>	Nagoya Univ.	Reported the first AlGaIn-AlN Deep-UV LD grown by MOCVD. <sup>275</sup>
2022	M. Kushimoto <i>et al.</i>	Nagoya Univ.	Reported the first AlGaIn-AlN UV-C LD grown by MOCVD. <sup>276</sup>

require the creation of more electronic devices using MOCVD. The type and number blades of the Swiss Army Knife will be expanded, and the existing blades will become sharper and more effective and efficient in performing their designed functions.

**VIII. SUMMARY**

The pioneering work by Manasevit *et al.* on the MOCVD growth of a wide-variety of compound semiconductors, particularly, the III-Vs, in the late 1960s and early 1970s and much other subsequent work that I do not have the time and space to discuss in any detail, advanced the variety of capabilities and the State-of-the-Art for MOCVD-grown semiconductor materials. In the 1980s, MOCVD contributed strongly to a “Cambrian Explosion-Like” proliferation of III-V materials and devices. Many workers contributed to this explosion in research, development, and commercialization and expanded the MOCVD-grown III-V device world greatly, verifying that MOCVD is truly the “Swiss Army Knife of III-V Epitaxial Growth.” First demonstrated by Manasevit in 1968, it took only 32 years of research and development by many workers before MOCVD was employed, in 1983–2003, to create a ~\$40B company, SDL Inc.

I apologize in advance to many contributors and colleagues whose work I have not been able to discuss or cite. While it is impossible to describe all of the important and seminal work in this field in such a short paper, I am sure that the positive impact of MOCVD will continue to increase and that future researchers will add many important “capabilities” or “blades” to this Swiss Army Knife.

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**AUTHOR DECLARATIONS**

**Conflict of Interest**

The author has no conflicts to disclose.

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## Author Contributions

R. D. Dupuis performed all the roles in creating this manuscript and is the sole author.

**Russell D. Dupuis:** Conceptualization (lead); Formal analysis (lead); Writing – original draft (lead); Writing – review & editing (lead).

## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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- <sup>106</sup>The SS e-beam welding was done by Electron-Beam Engineering in Anaheim CA. They are still operating today in 2023.
- <sup>107</sup>ERDA was the U.S. Energy Research and Development Administration. It was created out of the U.S. Atomic Energy Commission in 1974 after the 1973 OAPC oil crisis to create alternate sources of energy for the USA. It was merged with the Federal Energy Administration to form the U.S. Department of Energy in 1977.
- <sup>108</sup>In 1975, I had developed a process for gold-plating all of the front and rear ferrules for Swagelok® fittings and the SS gaskets for the VCR fittings to prevent galling and a better seal. These were processed per my specification commercially by Anodyne Corporation, in Santa Anna, CA—they still are operating as a plating business in 2023. This greatly improved the leak-tightness of the gas piping system of the reactor—as measured by the “pressure rise” leak test.
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fire in 1967. MFCs became commercially available in the 1970s with the Tylan® FC-260, which for the first time gave semiconductor manufacturers automated control of process gasses into their tools, enabling great improvements in the throughput rates and yields.

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