INVITED PAPER

III–V Semiconductor Quantum-Well Devices Grown by Metalorganic Chemical Vapor Deposition

Metalorganic chemical vapor deposition and quantum-well heterostructures are critical technologies for light-emitting diodes. The history and development of these technologies is presented in this paper.

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ABSTRACT | The metalorganic chemical vapor deposition (MOCVD) technology for the growth of III–V compound semiconductors has been developed over the past 40+ years to become the dominant epitaxial materials technology for both research and production of light-emitting devices as well as many other optoelectronic devices. Because of the flexibility and control offered by this process, and the material quality produced by MOCVD, many important III–V devices have become commercially viable. This paper will describe the development of MOCVD for the growth of high-quality ultrathin layers and heterojunctions of III–V compound semiconductors, which are now commonly called "quantum wells (QWs)," and the optical devices, which exploit the unique properties of such layers, e.g., QW lasers and light-emitting diodes (LEDs).

KEYWORDS | Epitaxy; heterojunction lasers; light-emitting diodes (LEDs); metalorganic chemical vapor deposition (MOCVD); quantum-well (QW) lasers; semiconductor

The metalorganic chemical vapor deposition (MOCVD) epitaxial growth technology was first reported in the scientific literature in 1968 by Manasevit [1] at the North-American Aviation,[1] while similar processes and experimental results were previously described in the patent literature by other workers, e.g., [2]–[5], prior to 1967. Manasevit was primarily interested in technologies for the heteroepitaxial growth of III–Vs on insulating substrates, the analog of the silicon-on-insulator (SOI) and silicon-on-sapphire technology which he had also pioneered earlier [6]. Manasevit's early work on MOCVD, particularly his work over the period 1968–1975, established that MOCVD could be used to grow a wide variety of III–V (and II–VI and IV–VI) heteroepitaxial single-crystal semiconductor films on various insulating substrates. However, the results reported by Manasevit and several other researchers who became interested in MOCVD in that time period did not create much enthusiasm for this materials growth technology due to the limited quality of the films produced and the lack of any demonstration of device performance data, comparable to that reported for semiconductor devices grown by other more established III–V epitaxial materials technologies, in particular, liquid-phase epitaxy (LPE) and hydride and halide vapor-phase epitaxy (VPE).

In the mid-1970s, MOCVD was still a "research lab" process and many elements of the technology were still quite primitive with very few reliable commercial vendors of "high-purity" or even "purified" metalorganic sources. Also, the equipment commonly used for VPE at that time was also quite simple and consisted of SS tubing, valves,

Manuscript received December 3, 2012; accepted May 3, 2013. Date of publication August 22, 2013; date of current version September 16, 2013.
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Digital Object Identifier: 10.1109/JPROC.2013.2274919

[1]North American Aviation merged with Rockwell-Standard Corporation in 1967 and changed the corporate name to "North American Rockwell" and then later changed again to "Rockwell International." It is now owned by Boeing.

and various other components connected by poor performance compression fittings or, in some cases, by standard pipe threads sealed with Teflon tape. The gas flows were often controlled using "rotameter" float-type ball-in-glass-tube flow meters. Most of these components did not provide a good low-leak-rate vacuum-tight seal, so the MOCVD systems in that time frame tended to be prone to leaks and other forms of contamination. Since the metalorganics used in MOCVD are quite air sensitive and are almost all pyrophoric, the lack of "high-integrity" gas piping systems and "leak-free" metalorganic source packages often led to high levels of contamination of the epitaxial films with oxygen, Si, carbon, and many other impurities, which limited the epitaxial film quality of the materials grown.

I joined Rockwell International's Research and Development Group in the Electronics Research Center (ERC, Anaheim, CA, USA) in February 1975 and was initially tasked to characterize the MOCVD GaAs films grown on sapphire by Dr. Harold (Hal) Manasevit and his technician, William (Bill) Simpson. Electrical characterization by Hall-effect measurements was already established at the ERC, and I wanted to establish optical characterization as well. While I was limited in the financial support available to set up the optical characterization systems, I was able to find some surplus instruments within Rockwell, and the necessary power supplies, curve tracers, etc., for more detailed device characterization were also available in various other labs. Other groups within ERC had wire bonders, metal evaporators, lithography tools, etc., so I started to arrange to make p–n junctions, light-emitting diodes (LEDs), and solar cells, when the materials were available.

Most of Hal's interests were in the area of the heteroepitaxial relationships between semiconductor films and the insulating substrates, a field which he had pioneered, and not directly in the device area. Consequently, it became necessary for me to set up my own MOCVD system to grow "device structures" in order to evaluate the MOCVD-grown materials. Since the budget for this was again quite limited, I was fortunate to be able to be allowed to use components from Hal's extensive stock piles of valves, fittings, flow meters, pumps, H_2 purifiers, etc., from prior CVD systems that he and Bill had disassembled. There were five exhausted chemical processing hoods in the lab, and I took over one of the empty ones to set up my MOCVD system from spare parts (which, in most cases, I had to clean these parts to remove various contaminations) and with a few new components. As the research evolved, I was able to upgrade some of these used valves, etc., with new ones. I was able to start growing films with my "MOCVD-1" system by September 1975 and started to explore GaAs and AlGaAs growth.[2] I recognized Manasevit's prior demonstrations of the capability of MOCVD to grow Al-containing III–V films as a very useful characteristic since it is the only viable VPE technology that can handle Al in the vapor phase without serious issues with atomic Al reacting with the chamber walls.

The chamber in this MOCVD-1 system was not very sophisticated and followed the basic designs used earlier by Manasevit and Simpson. It consisted of a simple quartz reactor chamber, tapered at the top with a gas-deflector disk and attached to a Pyrex ground-glass reactor base seal. The base was sealed to the growth chamber with vacuum grease. The Pyrex base assembly was water cooled with Teflon seals on the bottom port to allow a ground-quartz rod (also sealed with vacuum grease) to extend into the growth chamber upon which a tube was placed with a small quartz disc, and three raised prongs upon which a SiC-coated graphite susceptor was placed. The quartz rod was rotated at ~10–20 r/min by a small electric motor attached to the rod by a Teflon tube coupling. The upper end of the quartz growth chamber was attached to a flexible stainless steel (SS) tube connected by an SS "UltraTorr" O-ring sealed coupling. While I was concerned that these seals were not ideal, I made the best effort I could to assemble a tight gas system and to clean the interior of all the valves, tubing, flow meters, etc. Since we did not have access to a He-mass spectrometer leak detector, I could only do "leak testing" using the "evacuate and pressure rise" test method using an oil-based vacuum pump, which was installed for rough pumping out the reactor and a Hg-vapor-based "high-vacuum" glass-chambered pump, which was used for evacuating the chamber after loading. These pumps were installed on the exhaust side of the reactor chamber.[3] Heating was provided by an external radio-frequency (RF)-generator coil coupled to the SiC-coated graphite susceptor upon which the substrate was placed. A photograph of this earliest MOCVD-1 system taken in October 1975 is shown in Fig. 1. A photograph of the growth chamber is shown in Fig. 2 with a (0001) sapphire substrate loaded for growth. Notice that this is a cold-wall system, but in this case, not water cooled.

In the first version of this MOCVD-1 system, I had a simple electrical solenoid-based switching system built for providing control of the pneumatic pressure lines which operated each SS bellows-sealed pneumatic valve (the "wood covered box" to the right in Fig. 1). These pneumatic valves provided "on–off" control of the H_2 gas flow into the metalorganic (MO) source cylinders (or "bubblers"), as well as the H_2 purge flows, main chamber H_2 flow, and hydride gas flow channels. The solenoid box was set up to switch sources into the main growth chamber inlet line (the "inject line") or the line which bypassed the reactor chamber (the "vent" line; i.e., a so-called "vent-run" mode

[2]In this paper, I will use the convention of using the variables x, y, and z to designate the alloy composition designations for these materials: $Al_xGa_{1-x}As$, $In_xGa_{1-x}As$, $In_xGa_{1-x}P_{1-z}As_z$, $In_y(Al_xGa_{1-x})_{1-y}P$, $Al_xGa_{1-x}N$, and $In_xGa_{1-x}N$. If no subscripts are given in the alloy chemical formula, it should be understood to refer to these designations.

[3]While I had the capability of using the chemical-series roughing pump in the exhaust line for "subatmospheric low-pressure" growth, I never operated this system in that mode because the atmospheric pressure growth presented no problems for AlGaAs epitaxy.

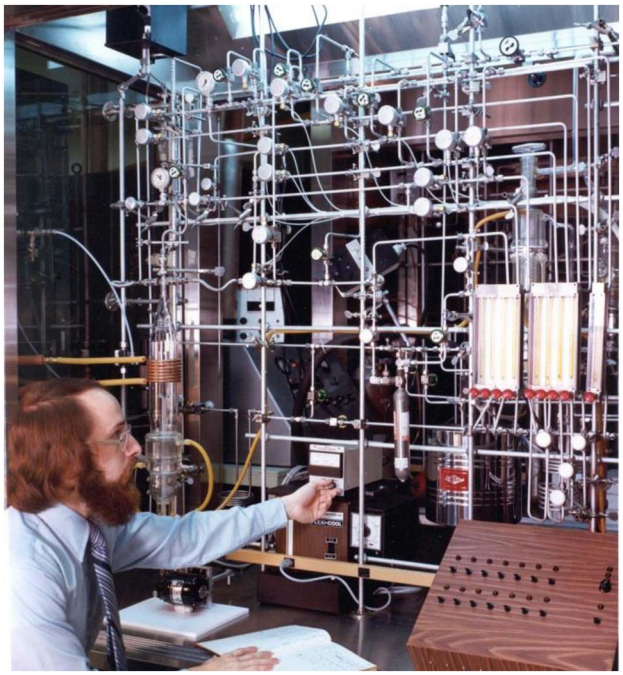

Fig. 1. *Photograph of me with the first MOCVD reactor I built at Rockwell International in 1975. (Photograph taken on October 20, 1975.)*

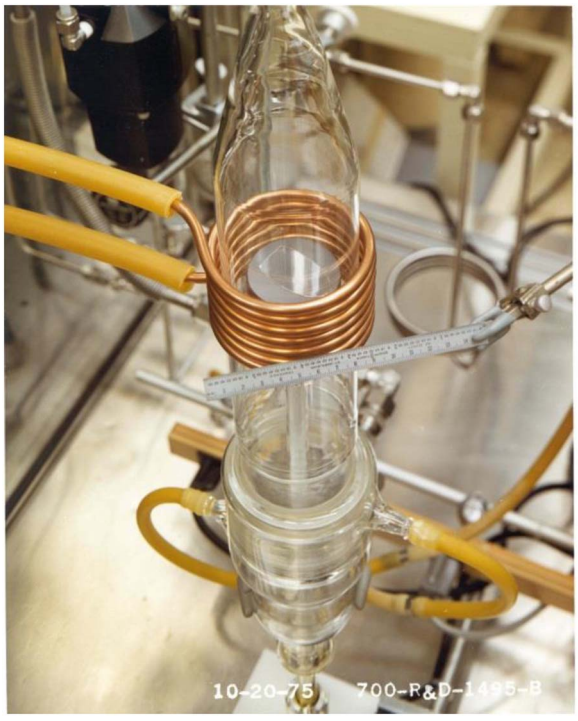

Fig. 2. *Photograph of the MOCVD reactor chamber with a large-area (0001) sapphire substrate loaded on the 2.0-in diameter SiC-coated graphite susceptor. (Photograph taken on October 20, 1975.)*

of operation) so that many source flows could be switched simultaneously. Gas flow rates were controlled by rotameter-type flow meters which were typically quite difficult to get to be leak tight. The MOCVD-1 system of Fig. 1 had only a "previously used" trimethylgallium [$Ga(CH_3)_3$, TMGa] source and the hydride arsine (AsH_3) installed. Later, I added trimethylaluminum [$Al(CH_3)_3$, TMAl] for AlGaAs growth, and the dopant sources diethylzinc [$Zn(C_2H_5)_2$, DEZn] for p-type growth, and hydrogen selenide (H_2Se) for n-type doping so that I could grow p–n heterojunction devices. Crystal growth was carried out at atmospheric pressure and at temperatures ~650 °C–750 °C, as measured by an optical pyrometer located outside the growth chamber.

In the earliest work in this reactor, I grew GaAs and $Al_xGa_{1-x}As$ films on (0001) sapphire substrates to calibrate the growth rates and the Al alloy compositions, x, as I could readily measure the layer thickness using optical reflectance and determine the alloy composition by determining the absorption edge of the film. I could also perform Hall-effect measurements on these films as the sapphire substrate was insulating. After such measurements, it was easy to etch the film off the substrate and use it again for another growth. By using sapphire substrates, I was able to determine the conditions necessary to grow a variety of GaAs and AlGaAs–GaAs devices. However, the basic question of the quality of the material could not be determined this way.

By early 1976, I had begun to grow films on GaAs substrates and was using semi-insulating Cr-doped GaAs to grow films for 300- and 77-K Hall-effect measurements. However, my photoluminescence (PL) system was not yet completed so I had to determine optimal growth conditions from mobility and surface morphology measurements. I found that the III/V ratio and the growth temperature were important parameters for producing the best AlGaAs films on GaAs. Since I had no independent standards, I just used a relative scale to determine the quality of the epitaxial films. I was concerned about the oxygen content of the $Al_xGa_{1-x}As$, especially for alloy compositions with $x > 30\%$. Rockwell's Anaheim Facility had a Physical Electronics "PHI" Auger electron spectrometer in another building, and I had a few samples analyzed in this system to establish the AlGaAs–GaAs interface abruptness and the [O], although this system was not "calibrated" for these measurements; I used a commercial GaAs substrate as a reference for [O]. From these measurements, I was fairly certain that I could make adequate heterojunction devices. Since I was using GaAs substrates, the $Al_xGa_{1-x}As$ alloy composition, x, could now be determined accurately by making X-ray diffraction measurements of the lattice parameter relative to GaAs.

By this time, my original MOCVD-1 system had been modified to include the TMAl, DEZn, and H_2Se sources as well as a more advanced "low-dead volume" bellows-sealed SS three-port manifold switching valves which provided a

much faster response time when the MO precursors were switched from "vent" to "run" mode. These equipment improvements were funded at a low level by the Rockwell International Internal Research and Development—IR&D funds.

The first device structure I grew was a GaAs:Zn/GaAs:Se p–n junction to check the diode I–V characteristics before I grew a complete solar cell. After alloying simple In–Sn and In–Zn contacts (cut from small alloy metal balls) to the wafer, I found that the I–V characteristics were quite good, exhibiting a nice "square" turn on and low reverse-bias leakage current, and the device responded well to illumination from a microscope light. With these data, I grew a complete $Al_{0.80}Ga_{0.30}As$:Zn/GaAs:Zn/GaAs:Se "window" heterojunction solar cell structure on a GaAs:Si n-type substrate. After making simple test devices, I took the samples outside in the sunlight to measure the approximate "air-mass 1.5" photoresponse since we had no solar simulator in the ERC at Rockwell. Using a digital multimeter, I measured the open-circuit voltage, the short-circuit current, and the fill factor, and found these values to be quite reasonable.

At this time, the U.S. Government was concerned about the effects of the 1973 Arab oil embargo on the economy of the United States, and in 1975, had established the Energy Research and Development Administration or ERDA (the precursor to the U.S. Department of Energy). This organization was interested in developing alternate energy sources, and issued a call for proposals for photovoltaic research. Thus, the timing of my initial MOCVD heterojunction solar-cell work was particularly propitious.

Because of the success of this early research on MOCVD solar cells, in 1976, I worked with others in the group at Rockwell to submit a proposal to ERDA for further solar-cell research, and I proposed to construct and improved MOCVD system and to purchase more test and measurement equipment, including a solar simulator and an Ar-ion laser for a photoluminescence (PL) system. We were successful in getting this proposal funded, and I started in earnest to construct a second, more advanced MOCVD system in 1976. The ERDA-funded research program was focused on the MOCVD growth of III–V solar cells on "low-cost substrates, e.g., high-temperature glass, Mo metal, Mo-coated glass composites, etc., but this work was primarily done in the MOCVD-1 system. The new second MOCVD system, MOCVD-2, was constructed for the growth of "high-quality" AlGaAs–GaAs heterostructures and was first devoted to AlGaAs–GaAs solar cells and then to AlGaAs–GaAs injection lasers.

This MOCVD-2 system was much more advanced and was, to my knowledge, the first computer-controlled MOCVD system ever constructed. The system employed many new components, including SS Nupro Model4H bellows-sealed manual valves, TylanModel260 electronic mass flow controllers, and special Hoke three-port, low-dead volume bellows-sealed switching valves with face-sealing fittings using metal gaskets (VCR type). In addition, I designed and built an improved reactor control system using a 16-channel Tylan electronic sequencer. Finally, I designed and built a gas distribution system with the TMGa, TMAl, and DEZn metalorganic source "bubblers" attached to the low-volume valves to provide for rapid switching. The electronic sequencer contained an optical card reader and could be programmed with standard key-punched "IBM cards" to load a run recipe containing as many as 16 steps into memory for later execution with possible loops. Again, I was very concerned about the effects of oxygen on the growth of the AlGaAs films, and although most of the SS tube fittings were Swagelok, I used careful cleaning, assembly, and sealing techniques to realize the best possible leak integrity of the system.

The "standard" MO source bubblers available at the time from commercial vendors were all-pipe-thread sealed 304 SS cylinders with similar low-quality "packed" valves with Teflon-taped pipe-thread input and output connections. Because these cylinders were prone to leaking at the pipe-thread joints and valve stems, the contents were potentially subject to contamination due to the diffusion of water into the valve. This was especially problematic since the MO sources are all pyrophoric and the bubblers were typically immersed in a "constant-temperature" bath containing a liquid, and ice bath in the case of TMGa, to control the vapor pressure. To improve on this packaging of the MOs, I designed and built special all-welded 316 SS metalorganic source cylinders using Nupro 316 SS bellows-sealed valves and electron-beam welding so that the alkyls would stay as pure as possible while they were used. I transferred commercially supplied metal organics into these vessels using a gravity-feed transfer procedure under high vacuum. To my knowledge, these are the first high-purity all-welded metal organic source cylinders ever fabricated. A photograph of the MOCVD-2 system shortly after it was completed in January 1977 is shown in Fig. 3. The photograph shows the system controls on the right and the growth chamber on the left. The TMGa source is in the Dewar with ice in the center of the picture; the TMAl is the larger bubbler on the right of the TMGa; and the DEZn is in the smaller bubbler to the left of the TMGa. These later two sources were used "at room temperature" with no active temperature control; consequently, if the air conditioning changed in the lab, so did the vapor pressures. All of these bubblers on MOCVD-2 employed my new e-beam welded 316 SS design. A schematic diagram of this MOCVD-2 reactor is shown in Fig. 4.

With the completion of the MOCVD-2 reactor, my research focused on AlGaAs–GaAs laser and solar-cell growth on GaAs substrates. By May 1977, I had calibrated the optimized growth conditions for AlGaAs, as well as doping levels and growth rates for these films. In early May 1977, I grew the first $Al_{0.8}Ga_{0.2}As$–GaAs "window" solar cell wafer in this system and found excellent device I–V and photoresponse characteristics. [7] Also in May 1977,

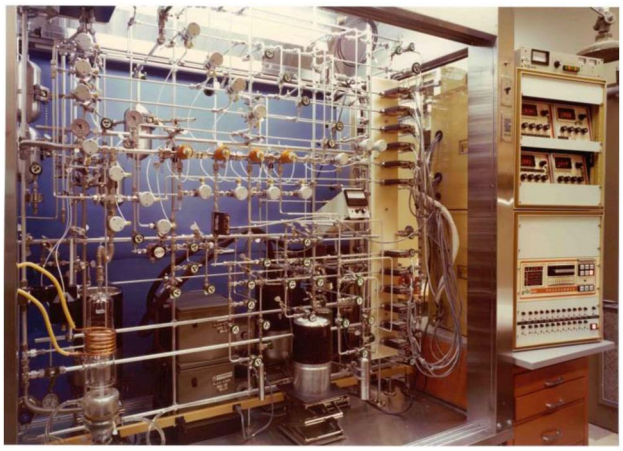

Fig. 3. *Photograph of the second MOCVD reactor I built at Rockwell in 1976. This system is "computer controlled" and contains a more advanced low-dead-volume gas-switching manifold. (Photograph taken on January 10, 1977.)*

I grew the first complete simple AlGaAs–GaAs double-heterostructure (DH) laser structure following the designs currently described in the literature being grown by LPE. These structures typically employed $Al_xGa_{1-x}As$ x $\sim$ 0.3 cladding layers and a GaAs active region $\sim$0.3 μm thick. I fabricated the lasers by thinning a portion of the wafer and then asked a Rockwell technician to evaporate ohmic contact metallization to the n- and p-sides of the wafer. After alloying these contacts, I cleaved laser bars and sawed or cleaved individual broad-area devices. The first broad-area laser chips I tested lased pulsed at 300 K so I was very happy with this first laser wafer growth. I found many devices which lased at threshold current densities (J_{th}) $\sim$3 kA/cm^2, which was not too much higher than similar typical LPE-grown lasers [8]. In my first paper on MOCVD-grown lasers, I stated that "epitaxial layers as thin as 500 Å are reproducibly grown in with a thickness uniformity of $\pm$3% in our present reactor" and speculated that MOCVD could be expanded to grow "GaAlAs/GaAs heterostructure films over $>$ 200 cm^2 of substrates in a single deposition run." These statements would later be proven to be understatements of the capabilities of the MOCVD process for a wide variety of III–V semiconductors, not just AlGaAs–GaAs devices.

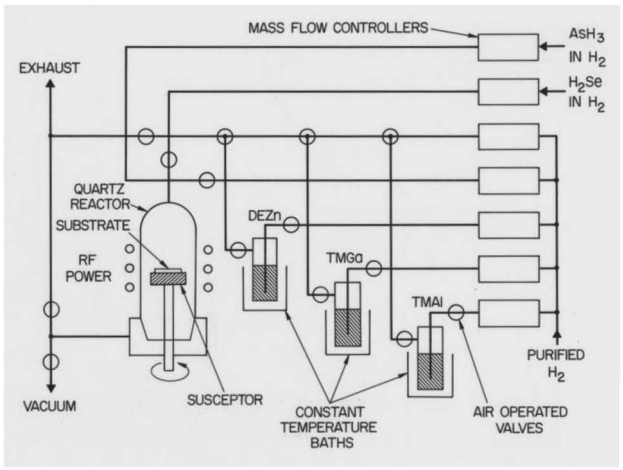

Fig. 4. *Schematic diagram of the MOCVD system used for laser growth.*

When I reported this work on the first MOCVD-grown lasers [9] and solar cells [10] as "late news papers" at the June 1977 Device Research Conference at Cornell University (Ithaca, NY, USA), I discovered that my Ph.D. advisor, Prof. Nick Holonyak, Jr., and his graduate students from the University of Illinois at Urbana–Champaign (UIUC, Urbana, IL, USA) were also reporting in a late news paper the LPE growth of InGaAsP/InP diode lasers with ultrathin active regions which exhibited "quantum-size effects" and which operated in pulsed mode at 77 K [11], [12]. After our papers were presented, Prof. Holonyak and I got together informally one evening and discussed our work. He was surprised to hear that my MOCVD reactor was computer controlled and that it was designed to grow very thin layers $\sim$50 nm thick. I was surprised to hear that he had devised a way to use LPE to grow complex quaternary GaAlAsP ultrathin layers, as thin as $\sim$50 nm lattice-matched to GaAs. Holonyak had been trying for years to get researchers at Monsanto Electronic Materials Corporation (St. Peters, MO, USA), where he was a consultant on LEDs, to arrange to grow thin layers by hydride VPE, but he was never successful in getting them to commit to do this, owing to their production demands for GaAsP VPE materials for red, orange, and amber LEDs [13]. At Nick's suggestion, we quickly worked out an informal collaboration between my work at Rockwell and his group's work at UIUC to explore MOCVD for the growth of lasers with ultrathin active regions.

After the DRC, I returned to my lab and began further work on AlGaAs DH lasers with AlGaAs active regions. This was done to establish that the MOCVD process was capable of producing "high-optical-quality" AlGaAs layers as well as GaAs films. At this time, many researchers were still very skeptical about claims that MOCVD could produce low-impurity Al-containing films, and oxygen was of particular concern. In order to establish the quality of AlGaAs, it would be necessary to demonstrate an AlGaAs DH laser diode with AlGaAs active regions, which I did in August 1977 [14].

My collaboration with Holonyak's group was also a high priority so I worked on establishing the growth conditions for ultrathin AlGaAs–GaAs quantum-well (QW) layers. By the end of October 1977, I had grown several AlGaAs–GaAs single-QW laser wafers which had been sent to Holonyak's group for device processing. Our first paper on QW laser diodes operating at 300 K was submitted on November 10, 1977 [15]. This paper was the first to refer to such devices as "QW lasers," and the name has stuck. It

was also the first report of room-temperature operation of a QW injection laser. I also grew multiple-quantum-well (MQW) lasers and explored the optimum number of QWs and cladding layer compositions. A few months later, in December 1977, I demonstrated continuous-wave (CW) 300-K operation of AlGaAs–GaAs DH lasers [16]. We now set out to explore CW operation of AlGaAs–GaAs QW lasers.

The electronic properties of ultrathin semiconductor layers has been studied since at least 1955 when the properties of thin surface space-charge layers in Si were investigated by Bardeen and Schrieffer at UIUC [17] and in 1967 by Stern and Howard at IBM [18], [19]. These "spontaneously formed" quantum structures were of interest for many reasons, one of them being understanding the effect of surface states on bipolar and field-effect transistors in Ge and Si.

The epitaxial growth of ultrathin layers of III–V semiconductors was developed first by molecular-beam epitaxy (MBE). MBE was developed for GaAs growth by Cho at AT&T Bell Laboratories and was first reported in 1970 [20] and for $Al_xGa_{1-x}As$ $(0.1 \leq x \leq 0.47)$ growth in 1971 [21]. In 1970, Esaki and Tsu at the IBM Research Center proposed a new class of "engineered materials" using the creation of artificially constructed ultrathin layers of semiconductors having different energy gaps [22]. Esaki was primarily interested in the *electrical properties* of these structures, in particular, the electron tunneling characteristics of superlattices [22], [23]. In 1971, Cho responded to this IBM work with a paper describing MBE as an ideal choice for producing such superlattices, but he only described the growth of a single AlGaAs–GaAs heterojunction in this paper [24]. In 1973, Chang *et al.* at IBM reported the computer-controlled MBE growth of a complete AlGaAs–GaAs superlattice with 100 layer pairs of GaAs "wells" ($L_z = 6$ nm)[4] and $Al_{0.5}Ga_{0.5}As$ "barriers" ($L_B = 1$ nm) and studied the electrical properties of these structures (see [25]; to my knowledge, this paper, describes the first computer-controlled III–V epitaxy system). In 1974, Chang *et al.* demonstrated the MBE growth of AlGaAs ($L_B = 8$ nm) resonant tunneling barriers surrounding a GaAs ($L_z = 5$ nm) well and reported the observation of unique I–V characteristic for these "resonant tunneling" structures [26]. This set the stage for other workers to become interested in the growth and characterization of the optical properties of ultrathin periodic III–V compound semiconductor "superlattices" and heterostructures. Also in 1974, Dingle *et al.* working at Bell Labs (Murray Hill, NJ, USA), reported the growth and characterization of AlGaAs–GaAs ultrathin heterostructures grown by MBE, and they reported the optical absorption spectra of a few samples with 50 pairs of AlGaAs ($x = 0.20$, $L_B > 25$ nm barriers)/GaAs ($L_z = 48$–21 nm wells) but no optical emission spectra were reported [27].

In 1975, van der Ziel *et al.* at Bell Labs reported the low-temperature laser operation from quantum states in ultrathin $Al_xGa_{1-x}As$--GaAs multilayer heterostructures [28]. The structures consisted of 50 pairs of $Al_{0.2}Ga_{0.8}As$ ($L_B = 24$ nm)/GaAs ($L_z = 8$ nm) heterostructures and optically pumped lasing was reported only at 15 K at input power density thresholds of $\sim$200 kW/cm^2, or an "equivalent current density" of $\sim$120 kA/cm^2. While these samples had GaAs QWs in the active region, these results were disappointing to the authors because "the observed thresholds were very high and gave no indication of the beneficial effects that one might expect from the modified density of states of these structures" (see paragraph 1 of [29, p. 4509]).

One year later, in 1976, Miller *et al.* at Bell Labs reported laser oscillations from four MBE-grown epitaxial wafers having very thin GaAs–AlGaAs multilayer structures with 25–50 pairs of $Al_xGa_{1-x}As$--GaAs thin barrier layer shaving Al compositions of $0.2 \leq x \leq 0.3$ and GaAs wells with 9.2 nm $\leq L_B, L_z \leq$ 18.8 nm [29]. The optical properties of these four multilayer structures were studied over the temperature range 6 K $\leq T \leq$ 300 K and compared with LPE- and MBE-grown standard DH wafers. They reported the observation of stimulated emission at 300 K for cleaved samples with Fabry–Perot cavities that were $\sim$1 mm long, from only two of the four MBE-grown "multilayer" structures (samples with 50 and 100 superlattice pairs) at relatively high optical-pumping thresholds. The stimulated emission thresholds for the MBE-grown thin multilayer structures were two to three times that of the "standard" DH samples. The optical pumping powers for this work were not given. However, the authors estimated that the "equivalent" threshold current densities corresponding to these pumping conditions were $\sim$4.1–21 kA/cm^2 at 6–8 K and $\sim$75–333 kA/cm^2 at 300 K.[5] No injection devices were reported. From the fact that these samples had so many superlattice pairs (i.e., a large gain volume), and such a high threshold for a "long-cavity" sample, it seems clear that the overall optical gain per superlattice period or, more specifically, per GaAs QW, was quite small.

As I mentioned above, Holonyak at UIUC had been interested in the optical properties of ultrathin semiconductor heterostructures well before 1977 and had attempted to get Monsanto to set up an apparatus to grow such structures by VPE but could not get the management to agree with this plan. Holonyak's work to create such structures by LPE was related to the fact that this "simple" LPE technology was readily available in his lab. He felt that he could modify the LPE system to accomplish the very challenging task of creating lattice-matched InGaAsP–InP

[4]In this paper, I will use L_z for the thickness (in the z-direction) of the QW and L_B for the thickness of the QW barriers.

[5]Note that these pumping power density values were estimates of how much of the $\lambda = 723.5$ nm pump laser input was absorbed by the 9.2-nm GaAs layers, not the actual input pump power incident on the sample surface which was much higher. See [29, p. 4510].

thin layers to study such samples. Holonyak told his students: "The crystal does not know how it was grown!" and so it made sense to give it a try. Holonyak's first LPE-grown diode lasers with multiple-thinlayer active regions operated pulsed at 77 K. These LPE-grown structures had ~20 pairs of $In_xGa_{1-x}P_{1-z}As_z$ ($x = 0.12$, $y = 0.26$, $L_z \sim 50$ nm) QWs and InP ($L_B \sim 50$ nm) barriers and lased at $\lambda \sim 1.05$ μm [11], [12]. These are the first non-AlGaAs-based QWs ever grown. The 77-K threshold current densities were quite low: $J_{th} \sim 890$ A/cm^2. These were the *first QW laser diodes*, although the authors did not explicitly use this term to describe their results.

In October 1977, as I have described, I had grown several $Al_{0.52}Ga_{0.48}As$–GaAs single-quantum-well (SQW) laser diodes, as we now began to call them, with QWs as narrow as ~20 nm. In our first paper, we reported MOCVD 300-K pulsed SQW diode lasers that exhibited relatively low thresholds of $J_{th} = 3$ kA/cm^2 for diodes with a cavity length of only ~170 μm [15]. These diodes showed very clear emission from QW states and, in fact, were the first diodes to exhibit clear stimulated emission from heavy- and light-hole states.

In January 1978, I grew GaAs SQW laser structures with $L_z \sim 20$ nm that Holonyak's team optically pumped to active 300-K CW operation at input powers (at the sample surface) of ~5 kW/cm^2 [30]. These structures exhibited pronounced quantum-size effects and operated as lasers on the first, second, and third quantum states, clearly demonstrating the pronounced effects of quantum confinement of the carriers in the SQW active region. These were the first 300-K CW QW lasers.

In early 1978, I also began to study the MOCVD growth of $Al_xGa_{1-x}As$–GaAs diode lasers with nonplanar active regions, and, in June 1978, I demonstrated a novel "channel-guide" laser grown over a nonplanar GaAs substrate. The undoped GaAs active region was only ~64 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. This work established that MOCVD could grow nonplanar thin active regions and, ultimately, this idea was used to grow nonplanar QW laser diodes with controlled output beam shapes.

After this, I began to work on improving the QW diode laser structures to reduce the 300-K threshold current densities. One such obvious modification would be in increasing the number of QWs in the active region to increase the overall gain volume and to improve the overlap of the gain medium with the optical field in the cavity. The first step was to grow and characterize the MQW active regions and evaluate their optical properties. The first low-threshold CW optically pumped 300-K QW lasers were made from MOCVD MQW wafers I grew in June 1978 [31]. The active region of these structures consisted of four pairs of $L_z \sim 8$ nm GaAs wells and $L_B \sim 8$ nm AlGaAs $x = 0.35$ barriers. The lasers were fabricated at UIUC using Holonyak's optically pumped laser wafer-thinning process (a secret recipe) and then were cleaved into laser bars with cavity lengths 10–100 μm long. These lasers operated CW under optical pumping in the temperature range 300–337 K at photoexcitation levels as low as ~1.2 kW/cm^2 or an estimated corresponding current density of J_{th} ~500 A/cm^2. These relatively low input powers gave us a reason to believe we could make a 300-K CW MQW *injection laser*.

The first CW 300-K QW laser diodes were fabricated from wafers I grew in MOCVD-2 in September 1978 [32]. These were SQW laser diodes with an $L_z \sim 20$-nm-thick GaAs QW and AlGaAs $x \sim 0.52$ cladding regions. The J_{th} was ~2.4 kA/cm^2 for diodes with a cavity length ~275 μm and the lasing spectra exhibited pronounce quantum-size effects, with laser emission at wavelengths corresponding to the quantum states in the QWs. We also reported a very high external differential quantum efficiency $\eta_{\text{diff}} \sim 80\%$, which was much larger than that observed for conventional DH lasers and attributed this improved performance to the use of the QW active region.

To many researchers, the concept that MOCVD could be used to grow films as thin as MBE was a great surprise, and often we experienced reviewers and others at conferences who were skeptical and wanted proof that the MOCVD QWs were really thin and really existed. So Holonyak and his team at UIUC developed a process of precise one-degree angle lapping to expose the MQW active regions, and then they measured the resulting cross-section bevel in a scanning electron microscope (SEM) to determine the thickness. This work was published in 1979 [33]. Later in 1979, working with Spicer's group at Stanford University (Stanford, CA, USA), we showed that MOCVD-grown AlGaAs ($x = 0.55$, $L_B \sim 6$ nm)/GaAs ($L_z \sim 8.6$ nm) MQW heterostructures were very abrupt by the direct measurement of the interface atomic profiles using Auger electron spectroscopy (AES) combined with sputtering [34]. The AES data showed that the 10%–90% interface width was ~1.7–2.0 nm for these QW heterostructures. Furthermore, the data showed that all three of the QWs and QWBs were uniform in thickness and alloy composition. These heterojunction interface width results were actually better than those reported in 1974 by Ludeke *et al.* from IBM for MBE-grown AlGaAs ($x = 0.25$, $L_B = 5$ nm)/GaAs ($L_z = 5$ nm) superlattices [35] and comparable to the interface widths reported later in 1979 by Spicer's group at Stanford for MBE-grown superlattice structures of AlGaAs ($x = 0.50$, $L_B = 10$ nm)/GaAs ($L_z = 10$ nm) where they measured a 10%–90% interface width ~1.3 nm [36], [37]. These 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.

By April–May 1979, I had developed improved MQW lasers and in late May, we demonstrated CW operation of $Al_xGa_{1-x}As$--GaAs MQW diodes at 300 K. These devices employed six pairs of GaAs QWs with $L_z \sim 12$ nm and

AlGaAs x = 0.30 barriers with $L_B \sim 12$ nm. CW values of $J_{th} \sim 1.6$ kA/cm^2 for diodes with cavity length of 489 μm were demonstrated with high external differential quantum efficiencies $\eta_{\text{diff}} \sim 85\%$ and exhibited single-longitudinal-mode operation over a wide current range, properties we came to associate with QW lasers [38].

One remaining big question, and one I was asked all the time at conferences, was: "What is the reliability of MOCVD-grown lasers?" I had no support at Rockwell for establishing laser life-testing equipment; in fact, I only had one stable precision constant-current source to use for CW laser diode testing and no temperature control system, facet coatings, proton bombardment, etc., to make and test reliable stripe-geometry lasers. Nevertheless, I set about to determine the life time as best I could under the existing primitive conditions. I published the first reliability data for QW lasers and the first such data for any MOCVD-grown laser in May 1979 [39]. In this work, I constructed several oxide-defined stripe-geometry lasers with a six-pair AlGaAs (x = 0.30, $L_B = 12$ nm)/GaAs ($L_z = 12$ nm) MQW active region, and I set up one laser diode at (uncontrolled) "room temperature" at constant current (CW) well above the threshold and periodically measured the output power. Over the 700 h of operation of this test, only a small change in the output power was measured. While this was not much data, it demonstrated that MOCVD-grown MQW lasers could be quite reliable and, with proper advanced device processing and packaging, these materials could potentially be viable in high-reliability applications, not just for "flash bulbs."

Working in collaboration with Holonyak's team at UIUC, in 1979, we studied the temperature dependence of the threshold current for AlGaAs–GaAs MOCVD MQW lasers and, in 1980 [40], we published data showing that the temperature sensitivity for SQW and MQW lasers was much less than that measured for "typical" DH lasers with characteristic temperatures T_0 as high as 437 °C. This result we explained in terms of the modified step-like density of states in a QW active region, which alters the phonon–electron interaction during laser operation.

In November 1979 (over one year after the first MOCVD QW lasers were reported), Tsang at Bell Labs reported the first MBE-grown QW lasers [41]. These lasers employed MQW active regions containing 14 pairs of AlGaAs (x = 0.27, $L_B = 13.0$ nm)/GaAs ($L_z = 13.6$ nm) layers. The average pulsed threshold current densities for 375 μm × 200 μm diodes was $J_{th} \sim 2$ kA/cm^2. It was not clear why Tsang used so many QWs in the active region. However, these were the first reported MBE-grown QW diodes and first to operate at 300 K, but only in pulsed mode.

I left Rockwell International for AT&T Bell Labs' Research Division (also known as Area 10) at Murray Hill, NJ, USA, in September 1979, and was assigned lab space on the third floor of Building 1 in the C Section. Working with Bell Labs facilities engineers, it took me about two years to design and build a clean room MOCVD lab there and when this was finally completed, I designed and constructed a new MOCVD system for AlGaAs growth. By 1982, I had reestablished my MOCVD materials growth processes and started to grow AlGaAs–GaAs QW lasers again. In 1982, I made the first MOCVD-grown laser diodes at Bell Labs.

At Bell Labs, the emphasis was on "reliability" and the Murray Hill Laser Development Group (in Area 20) had been exploring the production of AlGaAs telecom lasers by LPE for many years. By the time I arrived, they also were planning to develop MBE and MOCVD to determine whether these technologies offered any advantages of LPE for the production of diode lasers for the Bell System.

Consequently, it became even more important for me to establish the reliability of MOCVD MQW lasers at a "real telecom performance level." At Bell Labs, I worked on the MOCVD growth of more advanced MQW laser structures, e.g., the graded-index, separate-confinement heterostructure, (GRIN–SCH) QW laser. These laser structures showed improved threshold and linearity, as well as a better control of the output beam. Working with Robert Hartman and Franklin Nash of the Bell Labs Laser Development Group, I grew some of these wafers for their proton-bombarded standard laser diode processing and after these devices were tested, we found extremely good reliability. These GRIN–SCH lasers had broad-area threshold current densities $J_{th} \sim 232$ A/cm^2 for 380 μm × 200 μm diodes and showed high external differential quantum efficiencies $\eta_{\text{ext}} \sim 50\%$–$75\%$. The fabricated proton-bombarded stripe-geometry lasers employed 5-μm-wide strips and 250-μm-long cavities with facet coatings. External differential efficiencies of $\eta_{\text{diff}} \sim 48\%$–$50\%$ were achieved, and the threshold current I_{th} was 49.2 mA with a sigma of 1.8 mA for 27 randomly selected lasers, showing very good uniformity of the MOCVD wafer. The reliability testing was performed at 70 °C at a constant output power of 5 mW. The current drive degradation rate was $\Delta I/I < 2.0\%$, which established that the extrapolated lifetime was $\sim 3.6 \times 10^6$ h, or about 400 years, at 25 °C. These very first MOCVD laser reliability data were now accepted by all researchers in the world as establishing the power and performance of the MOCVD process and the fact that MQW lasers could be of very high performance.

After these results were published, MOCVD became accepted worldwide for the production of advanced III–V semiconductor devices, and soon other materials were being explored. I began to convert my MOCVD system to InP-based materials growth and to develop my MOCVD system for InGaAsP quaternaries for long-wavelength (λ = 1.33–1.55 μm) lasers which were of growing interest to the Bell System for optical fiber communication systems.

Other workers, particularly in Japan, worked to develop MOCVD for AlGaAs MQW structures for visible red lasers and LEDs, and again, the power of MOCVD for the growth of MQW active regions was fully exploited. For

example, Kawai *et al.* from Sony (Tokyo, Japan) reported in November 1983 the growth of AlGaAs–GaAs MQW lasers with an active region consisting of five pairs of AlGaAs ($x = 0.35$, $L_B = 4$ nm)/AlGaAs ($x = 0.14$, $L_z = 15$ nm) QWs [42]. These lasers emitted at ~782 nm (just barely visible) and had threshold currents as low as $I_{th} \sim 50$ mA for a 250-μm-long diode.

The MOCVD growth at atmospheric pressure of epitaxial layers of many other III–V binary and ternary compound semiconductors besides GaAs had already been demonstrated by Manasevit *et al.* [43]–[45]. Using this same basic approach, but operating at reduced pressure, Duchemin *et al.* at Thomson-CSF (Neuilly-sur-Seine, France) in the 1978–1979 period, developed low-pressure MOCVD (LP–MOCVD) for the growth of GaAs-based [46] and InP-based structures [47]. This was particularly important for the growth of InP-based structures as this limited some of the prereactions between TMIn and PH_3. In 1980, following this pioneering work, Duchemin's group reported the 300-K operation of LP–MOCVD-grown InGaAsP–InP DH lasers with $J_{th} \sim 5.9$ kA/cm^2 for diodes with 400 μm × 125 μm cavities and emitting at $\lambda \sim 1.15$ μm [48]. In 1983, his group developed low-pressure MOCVD growth of $In_{0.63}Ga_{0.47}As$--InP lattice-matched superlattices. [49] Using LP–MOCVD, the Thomson-CSF group was also the first to grow InGaAsP–InGaAs–InP long-wavelength QW injection lasers in 1985 [50]. They reported 300-K pulsed operation at $I_{th} = 450$ mA for a separate-confinement heterostructure (SCH) QW laser diode with an $In_{0.53}Ga_{0.47}As$ QW ($L_z = 5$ nm) and $In_xGa_{1-x}P_{1-z}As_z$ ($x = 0.73$, $z = 0.59$) SCH layers emitting at $\lambda = 1.30$ μm grown by LP–MOCVD on an InP substrate.[6] InGaAsP–InP MQW lasers grown by MOCVD are now the "standard of the industry" for long-wavelength 1.33- and 1.55-μm laser diodes, as well as the sources and modulators for photonic integrated circuits (PICs) [51].

Other workers were exploring the MOCVD growth of wider bandgap InAlGaP quaternary alloy system lattice matched to GaAs in an effort to develop visible lasers and LEDs. There were particularly strong early efforts in 1984–1985 at Matsushita (Osaka, Japan) [52], NEC (Kanagawa, Japan) [53], and Toshiba (Kanagawa, Japan) [54].

However, the first "QW" laser structures in the InAlGaP system were grown in 1988 by MOCVD by Kuo *et al.* at Hewlett-Packard (San Jose, CA, USA) [55]. Working with Holonyak and his group at UIUC, these workers reported CW 300-K operation of optically pumped InAlGaP SQW heterostructures with $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ ($x = 0.22$, $L_z \sim 20$ nm) QWs emitting in the red at ~625 nm and pulsed at ~593 nm. In November 1988, the UIUC–HP groups, in a paper authored by Dallesasse *et al.*, reported 300-K CW operation of $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ MQW laser diodes. The active region consisted of four $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ ($x = 0.2$, $L_z = 20$ nm) QWs and three $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ ($x = 0.50$, $L_B = 10$ nm) barriers and diodes lased at $\lambda \sim 640$ nm (red orange) at a $J_{th} = 3.7$ kA/cm^2 for lasers with 375-μm-long cavities. These were the first true "visible" QW laser diodes ever constructed, and the results showed the power of the MOCVD process for the growth of ultrathin heterostructures, and the value of this important "wide-bandgap" quaternary system which could not effectively be grown by any other epitaxial process. Further development of the MOCVD growth of $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ QW lasers resulted in the commercial introduction of the "red laser" for digital video disk (DVD) applications [56], as well as ultrahigh-brightness AlInGaP MQW LEDs emitting in the red, orange, amber, and yellow spectral regions [57], [58].

Using MOCVD, QW lasers and LEDs in other even wider bandgap materials systems were also developed. As mentioned above, in 1971, Manasevit reported the MOCVD heteroepitaxial growth of GaN and AlN on (0001) sapphire substrates [45]. This work was basically ignored by many until 1986 when Akasaki *et al.* at Nagoya University (Nagoya, Japan) reported the MOCVD growth of "high-quality" GaN grown on sapphire using a low-temperature AlN buffer layer [59]. They also reported the growth of good crystalline quality AlGaN alloys and AlGaN–GaN heterostructures on sapphire [60]. This work led to the development of MOCVD growth for InGaN alloys on GaN/sapphire substrates in 1992 by Nakamura and Mukai at Nichia Chemical Industries (Tokushima, Japan) [61]. In this work, Nakamura *et al.* used a specialized version of MOCVD growth at atmospheric pressure—the so-called "two-flow" process—for InGaN alloys and GaN heteroepitaxy on sapphire substrates, and they demonstrated record efficiency for InGaN-based QW LEDs emitting in the blue spectral region. In 1993, Nakamura *et al.* reported the MOCVD growth of high-power InGaN–GaN SQW LEDs emitting at $\lambda \sim 411$–420 nm (violet) with an InGaN QW having $L_z = 10$ nm. The output power of these devices at 300 K was 90 μW and a total external quantum efficiency of $\eta_{ext} = 0.15\%$ was measured at 20-mA forward current. These were the first reported III–N QW devices, and this work set the stage for further development of blue and green InGaN–GaN MQW LEDs. In 1994, Nakamura *et al.* reported even higher output powers for MOCVD-grown $In_{0.06}Ga_{0.94}N$–$Al_{0.15}Ga_{0/85}N$ SQW LEDs with devices emitting output powers of 1500 μW and exhibiting an $\eta_{ext} = 2.\%$ at 20 mA [62].

In March 1994, Akasaki's team reported the first 300-K stimulated emission from MOCVD-grown optically pumped AlGaN–InGaN DH structures [63]. These DH structures were grown on sapphire using an AlN buffer layers and consisted of an $In_xGa_{1-x}N$ single active region ($x = 0.09$, $t = 0.34$ μm, and 0.1 μm) and $Al_xGa_{1-x}N$ ($x = 0.17$, $t = 0.34$ μm) cladding layers. These optically pumped lasers operated pulsed at an input power of ~0.13 MW/cm^2 and emitted at $\lambda \sim 402.5$ nm. While these

[6]Curiously, no laser spectra were shown in this paper.

thresholds were quite high, this work demonstrated that the InGaN alloy system could support 300-K stimulated emission and lasing.

In November 1995, Akasaki's team reported the first III–N MQW diode lasers [64]. The MOCVD-grown laser structure had ~10 pairs of GaN barriers ($L_B \sim 7.5$ nm) and InGaN QWs ($x = 0.07$, $L_z = 2.5$ nm) and $Al_xGa_{1-x}Nx = 0.1$ n- and p-type cladding regions grown on sapphire. Laser devices with a cavity length of 1.0 mm were fabricated and tested. These lasers operated pulsed at 300 K and lased at $\lambda \sim 400$ nm at a threshold current of 10 mA corresponding to $J_{th} \sim 1.0$ kA/cm^2.

Nakamura *et al.* at Nichia reported their first InGaN-based QW injection lasers a few months after Akasaki in January 1996 [65], [66]. These devices were grown by atmospheric pressure MOCVD on sapphire using the "two-flow" process and employed a seven-QW MQW active region consisting of InGaN ($x = 0.05$, $L_z = 2.5$ nm) QWs and InGaN ($x = 0.2$, $L_B = 5$ nm) barriers. Laser bars with 670-nm cavity lengths were facet coated and operated at 300 K in pulsed mode at $J_{th} \sim 4.6$ kA/cm^2, and the peak output power was 8 mW per facet at a peak diode current of ~180 mA with a forward voltage of 22 V. While these forward operating voltages were very high, and CW operation could not be achieved, the data clearly showed that MOCVD InGaN–GaN MQW lasers were going to have a very bright future. Additional work, first at Nichia and then by many other researchers all over the world, has resulted in lower thresholds for MOCVD-grown III–N lasers, longer and shorter wavelengths (as long as $\lambda = 533.6$ nm [67] and as short as $\lambda = 336$ nm [68]), and better quantum efficiencies, lower operating voltages, higher yields for both lasers and LEDs, and, as a direct result, the great expansion of the purchase and use of large-area commercial III–N MOCVD systems.

At this time in 2012, the active regions of all of the high-brightness ultraviolet, violet, blue, cyan, and green InAlGaN-based LEDs (and laser diodes) are MQW heterostructures grown by MOCVD, as are all of the III–N laser diodes in commercial production. Today, commercial MOCVD systems with a capacity of 19 wafers of 4-in diameter or five wafers of 8-in diameter in a single run (i.e., a total substrate area of ~1540 or ~1612 cm^2) have been developed to grow MQW structures with wells of thickness $L_z \sim 2$–5 nm for III–N LED applications.[7] The demand for these LED products for solid-state lighting is so high that many entirely new factories housing 100 MOCVD systems are being constructed. In addition, all of the visible LEDs and lasers in the InAlGaP quaternary alloy system, i.e., the red, amber, and yellow LEDs for signaling, e.g., traffic signals, automotive lighting, large-area digital displays, and the red lasers for DVD players, laser pointers, etc., are MQW devices grown by MOCVD. Virtually all of the commercial light-emitting devices in use today are manufactured by MOCVD and incorporate QW heterostructures in the active region. In addition, virtually all of the infrared injection lasers and LEDs operating at ~1.33 and ~1.55 μm used in telecommunication systems and many other applications are grown by MOCVD and incorporate QWs in the active region.

Even more complicated QW heterostructure lasers are grown by MOCVD. The quantum-cascade laser (QCL) was first invented by Kazarinov and Siris in 1971 [69], shortly after the pioneering suggestion of semiconductor superlattices by Esaki and Tsu in 1970 [22]. At the time, there was no epitaxial materials technology capable of growing such complicated structures. The first demonstration of QCLs was made in 1994 by Faist *et al.* at Bell Labs who used MBE to grow these complex AlGaAs–GaAs QW structures [70]. The first MOCVD-grown AlGaAs–GaAs [71] and AlInAs–InGaAs–InP [72] QCLs were reported by Roberts *et al.* in 2003. More recently, high-performance QCLs operating at $\lambda \sim 4$–12 μm, which use active regions containing $>$ 100 quantum-layer heterostructures in the AlInAs–InGaAs–InP system [73], have been grown by MOCVD and are in commercial manufacture [74].

In summary, the development of MOCVD deriving from the early pioneering work of Manasevit in 1968 has created an extremely flexible and powerful epitaxial growth technology, which has come to dominate the entire field of III–V epitaxial and heteroepitaxial growth today. The application of MOCVD to the growth of ultrathin QW structures resulted in the first demonstration of 300-K QW laser diodes and has provided the practical, reliable, and nearly ubiquitous materials technology for the development of many important compound semiconductor light-emitting devices. Currently, my "projections" from my first MOCVD laser paper in 1977 of MOCVD's capabilities for the uniform, reproducible growth III–V layers with $t \sim 50$ nm and substrate areas > 200 cm^2/run have been exceeded by a factor of more than eight! I expect that these current technology limitations will also be exceeded in the future. ■

Acknowledgment

The author would like to acknowledge the many contributions, and the constant support, and encouragement of Prof. N. Holonyak, Jr., and the collaborations with many of his former students who contributed so much to the work described here in the development of MOCVD for QW devices. It has been the author's great pleasure and a great honor to have published so many papers with Prof. Holonyak and his team at the University of Illinois at Urbana–Champaign (UIUC, Urbana, IL, USA). The author would also like to thank many past colleagues and collaborators, and research managers who made important contributions to this work. While there are too many to

[7]The AIXTRON Crius II–XL MOCVD system has a capacity of 19 4-in diameter wafers and the AIXTRON G5 HT MOCVD system has a capacity for five 8-in diameter wafers. See www.aixtron.com.

list, he would like to thank in particular Dr. J. Mee for hiring him at Rockwell International and for his early support of the author's MOCVD growth research. The author would also like to acknowledge the very kind sharing of advice, laboratory equipment, and space by Dr. H. Manasevit and W. I. Simpson at Rockwell, which was used in the construction of his first MOCVD system in 1975.

REFERENCES

[1] H. M. Manasevit, "Single-crystal gallium arsenide on insulating substrates," *Appl. Phys. Lett.*, vol. 12, no. 4, pp. 156–159, 1968.

[2] T. R. Scott, G. King, J. M. Wilson, and Standard Telecommunications and Cables, Ltd., "Improvements in or relating to the production of material for semi-conductors," British, Patent 778 383, Jul. 3, 1957.

[3] W. Miederer, G. Ziegler, R. Dötzer, and Siemens -Schuckertwerke, "Method of crucible-free production of gallium arsenide rods from alkyl gallium and arsenic compounds at low temperatures," U.S. Patent 3 226 270, Dec. 28, 1965.

[4] R. A. Ruehrwein and Monsanto Company, "Altering proportions in a vapor deposition process to form a mixed crystal graded energy gap," U.S. Patent 3 224 913, Dec. 21, 1965.

[5] R. A. Ruehrwein and Monsanto Company, "Production of epitaxial films of semiconductor compound material," U.S. Patent 3 312 570, Apr. 4, 1967.

[6] H. M. Manasevit and W. I. Simpson, "Single-crystal silicon on a sapphire substrate," *J. Appl. Phys.*, vol. 35, pp. 1349–1352, 1964.

[7] R. D. Dupuis, P. D. Dapkus, R. D. Yingling, and L. A. Moudy, "High-efficiency GaAlAs/GaAs heterostructure solar cells grown by metalorganic chemical vapor deposition," *Appl. Phys. Lett.*, vol. 31, no. 3, pp. 201–203, 1977.

[8] R. D. Dupuis and P. D. Dapkus, "Room-temperature operation of$Ga_{1-x}Al_xAs$/GaAs double-heterostructure lasers grown by metalorganic chemical vapor deposition," *Appl. Phys. Lett.*, vol. 31, no. 7, pp. 466–468, 1977.

[9] R. D. Dupuis and P. D. Dapkus, "Room-temperature operation of $Ga_{(1-x)}Al_xAs$/GaAs double heterostructure lasers grown by metalorganic chemical vapor deposition," *IEEE Trans. Electron Devices*, vol. ED-24, no. 9, pp. 1195–1196, Sep. 1977.

[10] R. D. Dupuis, P. D. Dapkus, R. D. Yingling, and L. A. Moudy, "High-efficiency GaAlAs/GaAs heterostructure solar cells grown by metalorganic chemical vapor deposition," *IEEE Trans. Electron Devices*, vol. ED-24, no. 9, pp. 1203–1204, Sep. 1977.

[11] A. Rezek, N. Holonyak, Jr., B. A. Vojak, G. E. Stillman, J. A. Rossi, D. L. Keune, and J. D. Fairing, "Liquid phase epitaxial InGaPAs multilayered heterojunction lasers exhibiting 'quantum size effects'," *IEEE. Trans. Electron Devices*, vol. ED-24, no. 9, p. 1204, Sep. 1977.

[12] A. Rezek, N. Holonyak, B. A. Vojak, G. E. Stillman, and J. A. Rossi, "LPE $In_{1-x}Ga_xP_{1-z}As_z$ ($x \sim 0.12$, $z \sim 0.26$) DH laser with multiple thin layer (< 500 Å) active region," *Appl. Phys. Lett.*, vol. 31, no. 4, pp. 288–290, 1977.

[13] N. Holonyak, Jr., private communication, Jun. 1977.

[14] R. D. Dupuis and P. D. Dapkus, "$Ga_{(1-x)}Al_xAs$–Ga(1- y)Al yAs room-temperature lasers grown by metalorganic chemical vapor deposition," *Appl. Phys. Lett.*, vol. 31, no. 12, pp. 839–841, 1977.

[15] R. D. Dupuis, P. D. Dapkus, N. Holonyak, Jr., E. A. Rezek, and R. Chin, "Room-temperature laser operation of quantum-well $Ga_{1-x}Al_xAs$–GaAs laser diodes grown by metalorganic chemical vapor deposition," *Appl. Phys. Lett.*, vol. 32, no. 5, pp. 295–297, 1978.

[16] R. D. Dupuis and P. D. Dapkus, "Continuous room-temperature operation of $Ga_{1-x}Al_xAs$–GaAs double-heterostructure lasers grown by metalorganic chemical vapor deposition," *Appl. Phys. Lett.*, vol. 32, no. 7, pp. 406–407, 1978.

[17] J. R. Schreiffer, "Effective carrier mobility in surface-space charge layers," *Phys. Rev.*, vol. 97, no. 3, pp. 641–646, 1955.

[18] F. Stern and W. E. Howard, "Properties of semiconductor surface inversion layers in the electric quantum limit," *Phys. Rev. Lett.*, vol. 163, no. 3, pp. 816–835, 1967.

[19] N. Holonyak, Jr., R. M. Kolbas, R. D. Dupuis, and P. D. Dapkus, "Quantum-well heterostructure lasers," *IEEE J. Quantum Electron.*, vol. QE-16, no. 2, pp. 170–185, Feb. 1980.

[20] A. Y. Cho, "Morphology of epitaxial growth of GaAs by a molecular beam method: The observation of surface structures," *J. Appl. Phys.*, vol. 41, no. 7, pp. 2780–2786, 1970.

[21] A. Y. Cho and S. E. Stokowsk, "Molecular beam epitaxy and optical evaluation of$Al_xGa_{1-x}As$," *Solid-State Commun.*, vol. 9, pp. 565–568, 1971.

[22] L. Esaki and R. Tsu, "Superlattice and negative differential conductivity in semiconductors," *IBM J. Res. Develop.*, vol. 14, no. 1, pp. 61–65, 1970.

[23] R. Tsu and L. Esaki, "Tunneling in a finite superlattice," *Appl. Phys. Lett.*, vol. 22, no. 11, pp. 562–564, 1973.

[24] A. Y. Cho. (1971). Growth of periodic structures by the molecular-beam method. *Appl. Phys. Lett.* [Online]. *19(11)*. Available: http://dx.doi.org/10.1063/1.1653775

[25] L. L. Chang, L. Esaki, W. E. Howard, and R. Ludeke. (1973). The growth of a GaAs–GaAlAs superlattice. *J. Vac. Sci. Technol.* [Online]. *10(11)*. Available: http://dx.doi.org/10.1116/1.1317919

[26] L. L. Chang, L. Esaki, and R. Tsu, "Resonant tunneling in semiconductor double barriers," *Appl. Phys. Lett.*, vol. 24, no. 12, pp. 593–595, 1974.

[27] R. Dingle, W. Wiegmann, and C. H. Henry, "Quantum states of confined carriers in very thin $Al_xGa_{1-x}As$–GaAs–$Al_xGa_{1-x}As$ heterostructures," *Phys. Rev. Lett*, vol. 33, no. 14, pp. 827–830, 1974.

[28] J. P. van der Ziel, R. Dingle, R. C. Miller, W. Wiegmann, and W. A. Nordland, Jr., "Laser oscillation from quantum states in very thin GaAs–$Al_{0.2}Ga_{0.8}As$ multilayer structures," *Appl. Phys. Lett.*, vol. 26, no. 8, pp. 463–465, 1975.

[29] R. C. Miller, R. Dingle, A. C. Gossard, R. A. Logan, W. A. Nordland, Jr., and W. Wiegmann, "Laser oscillation with optically pumped very thin GaAs–$Al_xGa_{1-x}As$ multilayer structures and conventional double heterostructures," *J. Appl. Phys.*, vol. 47, no. 10, pp. 4509–4517, 1976.

[30] N. Holonyak, Jr., R. M. Kolbas, R. D. Dupuis, and P. D. Dapkus, "Room-temperature continuous operation of photopumped MO-CVD $Al_xGa_{1-x}As$–GaAs–$Al_xGa_{1-x}As$ quantum-well lasers," *Appl. Phys. Lett.*, vol. 33, no. 1, pp. 73–75, 1978.

[31] N. Holonyak, Jr., R. M. Kolbas, W. D. Laidig, B. A. Vojak, R. D. Dupuis, and P. D. Dapkus, "Low-threshold continuous laser operation (300–337 K) of multilayer MO-CVD $Al_xGa_{1-x}As$–GaAs quantum-well heterostructures," *Appl. Phys. Lett.*, vol. 33, no. 8, pp. 737–739, 1978.

[32] R. D. Dupuis, P. D. Dapkus, R. Chin, N. Holonyak, Jr., and S. W. Kirchoefer, "Continuous 300 °K laser operation of single-quantum-well $Al_xGa_{1-x}As$–GaAs heterostructure diodes grown by metalorganic chemical vapor deposition," *Appl. Phys. Lett.*, vol. 34, no. 4, pp. 265–267, 1979.

[33] N. Holonyak, Jr., B. A. Vojak, R. M. Kolbas, R. D. Dupuis, and P. D. Dapkus, "Bevel cross sectioning of ultra-thin (100 A) III–V semiconductor layers," *Solid-State Electron.*, vol. 22, no. 4, pp. 431–433, 1979.

[34] R. D. Dupuis, P. D. Dapkus, C. M. Garner, C. Y. Su, and W. E. Spicer, "Abrupt $Ga_{1-x}Al_xAs$–GaAs quantum-well heterostructures grown by metalorganic chemical vapor deposition," *Appl. Phys. Lett.*, vol. 34, no. 5, pp. 335–337, 1979.

[35] R. Ludeke, L. Esaki, and L. L. Chang, "$Ga_{1-x}Al_xAs$ superlattices profiled by auger electron spectroscopy," *App. Phys. Lett.*, vol. 24, no. 9, pp. 417–419, 1974.

[36] C. M. Garner, F. C. Y. Su, Y. D. Shen, C. S. Lee, G. L. Person, W. E. Spicer, D. D. Edwall, D. Miller, and J. S. Harris, Jr., "Interface studies of $Al_xGa_{1-x}As$–GaAs heterojunctions," *J. Appl. Phys.*, vol. 50, no. 5, pp. 3383–3389, 1979.

[37] C. M. Garner, C. Y. Su, and W. E. Spicer, "Interface studies of $Al_xGa_{1-x}As$–GaAs heterojunctions," *J. Vac. Sci. Technol.*, vol. 16, no. 5, pp. 1521–1524, 1979.

[38] R. D. Dupuis, P. D. Dapkus, N. Holonyak, Jr., and R. M. Kolbas, "Continuous room-temperature multiple-quantum-well $Al_xGa_{1-x}As$–GaAs injection lasers grown by metalorganic chemical vapor deposition," *Appl. Phys. Lett.*, vol. 35, no. 7, pp. 487–489, 1979.

[39] R. D. Dupuis, "700 h continuous room-temperature operation of $Al_xGa_{1-x}As$–GaAs heterostructure lasers grown by metalorganic chemical vapor deposition," *Appl. Phys. Lett.*, vol. 35, no. 4, pp. 311–314, 1979.

[40] R. Chin, N. Holonyak, Jr., B. A. Vojak, K. Hess, R. D. Dupuis, and P. D. Dapkus, "Temperature dependence of threshold current for quantum-well $Al_xGa_{1-x}As$–GaAs heterostructure laser diodes," *Appl. Phys. Lett.*, vol. 36, no. 1, pp. 19–21, 1980.

[41] W. T. Tsang, C. Weisbuch, R. C. Miller, and R. Dingle, "Current injection GaAs–$Al_xGa_{1-x}As$ multi-quantum well heterostructure lasers prepared by molecular beam epitaxy," *Appl. Phys. Lett.*, vol. 35, no. 9, pp. 673–675, 1979.

[42] H. Kawai, O. Matsuda, and K. Kaneko, "High Al-content visible (AlGa) as multiple quantum well heterostructure lasers grown by metalorganic chemical vapor deposition," *Jpn. J. Appl. Phys.*, vol. 22, no. 11, pp. L727–L729, 1983.

[43] H. M. Manasevit and W. I. Simpson, "The use of metalorganics in the preparation of semiconductor materials," *J. Electrochem. Soc.*, vol. 120, no. 1, pp. 135–137, 1973.

[44] H. M. Manasevit, "The use of metalorganics in the preparation of semiconductor materials, III. Studies of epitaxial III–V Aluminum compound formation using trimethylaluminum," *J. Electrochem. Soc.*, vol. 118, no. 4, pp. 647–650, 1971.

[45] H. M. Manasevit, F. M. Erdman, and W. I. Simpson, "The use of metalorganics in the preparation of semiconductor materials, IV. The nitrides of aluminum and gallium," *J. Electrochem. Soc.*, vol. 118, no. 11, pp. 1864–1868, 1971.

[46] J. P. Duchemin, M. Bonnet, F. Kolesch, and D. Huyghe, "A new method for the growth of GaAs epilayer at low H_2 pressure," *J. Crystal Growth*, vol. 45, pp. 181–186, 1978.

[47] J. P. Duchemin, M. Bonnet, G. Beuchet, and F. Kolesch, "Organometallic growth of device-quality InP by cracking of in $(C_2H_5)_3$ and PH_3 at low pressure," *Inst. Phys. Conf. Ser.*, vol. 45, pp. 10–18, 1979.

[48] J. P. Hirtz, J. P. Duchemin, P. Hirtz, B. de Cremoux, and T. Pearsall, "$Ga_xIn_{1-x}As_yP_{1-y}$/InP D.H. laser emitting at 1.15μm grown by low-pressure metalorganic C.V.D.," *Electron. Lett.*, vol. 16, no. 8, pp. 275–277, 1980.

[49] M. Razeghi and J. P. Duchemin, "Low pressure-MOCVD growth of $Ga_{0.47}In_{0.53}As$–InP heterojunction and superlattices," *J. Vac. Sci. Tech. B, Micro. Proc. Phenom.*, vol. 1, no. 2, pp. 262–265, 1983.

[50] J. Nagle, S. Hersee, M. Razeghi, M. Karkowski, B. DeCremoux, and C. Weisbuch, "Properties of 2D quantum well lasers," *Surf. Sci.*, vol. 174, pp. 148–154, 1986.

[51] R. Nagarajan, C. H. Joyner, R. P. Schneider, Jr., J. S. Bostak, T. Butrie, A. G. Dentai, V. G. Dominic, P. W. Evans, M. Kato, M. Kauffman, D. J. H. Lambert, S. K. Mathis, A. Mathur, R. H. Miles, M. L. Mitchell, M. J. Missey, S. Murthy, A. C. Nilsson, F. H. Peters, S. C. Pennypacker, J. L. Pleumeekers, R. A. Salvatore, R. K. Schlenker, R. B. Taylor, H.-S. Tsai, M. F. Van Leeuwen, J. Webjorn, M. Ziari, D. Perkins, J. Singh, S. G. Grubb, M. S. Reffle, D. G. Mehuys, F. A. Kish, and D. F. Welch, "Large-scale photonic integrated circuits," *IEEE J. Sel. Top. Quantum Electron.*, vol. 11, no. 1, pp. 50–65, Jan.-Feb. 2005.

[52] Y. Ban, M. Ogura, M. Morisaki, and N. Hase, "MOCVD growth and characterization of $(Al_xGa_{1-x})_yIn_{1-y}P$/GaAs," *Jpn. J. Appl. Phys.*, vol. 23, no. 8, pp. L606–L609, 1984.

[53] K. Kobayashi, S. Kawata, A. Gomyo, I. Hino, and T. Suzuki, "Room-temperature CW operation of AlGaInP double-heterostructure visible lasers," *Electron. Lett.*, vol. 21, no. 20, pp. 931–932, 1985.

[54] M. Ishikawa, Y. Ohba, H. Sugawara, M. Yamamoto, and T. Nakanishi, "CW operation at−10 C for InGaAlP visible light laser diodes grown by MOCVD," *Electron. Lett.*, vol. 21, no. 23, pp. 1084–1085, 1985.

[55] C. P. Kuo, R. M. Fletcher, T. D. Osentowski, M. G. Craford, D. W. Nam, N. Holonyak, Jr., K. C. Hsieh, and J. E. Fouquet, "Stimulated emission in $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ quantum well heterostructures," *J. Crystal Growth*, vol. 93, pp. 389–395, 1988.

[56] K. Kadiowa, T. Motoda, T. Nishimura, S. Arimoto, H. Watanabe, T. Kamizato, K. Mizuguchi, and T. Murotani, "Multiple quantum barrier structures and their application to high-power visible laser diodes with strained InGaP active layers grown by MOCVD," *J. Crystal Growth*, vol. 124, pp. 757–762, 1992.

[57] M. G. Craford, N. Holonyak, Jr., and F. A. Kish, Jr., "In pursuit of the ultimate lamp," *Sci. Amer.*, vol. 284, no. 2, pp. 62–67, 2001.

[58] M. G. Craford, "Visible LEDs: The trend toward high power emitters and remaining challenges for solid state lighting," *Proc. SPIE—Int. Soc. Opt. Eng.*, vol. 4776, pp. 1–8, 2002.

[59] H. Amano, N. Sawaki, I. Akasaki, and Y. Toyoda, "Metalorganic vapor phase epitaxial growth of a high quality GaN film using an AlN buffer layer," *Appl. Phys. Lett.*, vol. 48, no. 5, pp. 353–355, 1986.

[60] M. R. H. Khan, Y. Koide, H. Itoh, N. Sawaki, and I. Akasaki, "Edge emission of $Al_xGa_{1-x}N$," *Solid-State Commun.*, vol. 60, no. 6, pp. 509–512, 1986.

[61] S. Nakamura and T. Mukai, "High-quality InGaN films grown n GaN films," *Jpn. J. Appl. Phys.*, vol. 21, pp. L1457–L1459, 1992.

[62] S. Nakamura, T. Mukai, and M. Senoh, "Candela-class high-brightness InGaN/AlGaN double-heterostructure blue light-emitting diodes," *Appl. Phys. Lett.*, vol. 64, no. 13, pp. 1687–1689, 1994.

[63] H. Amano, T. Tanaka, Y. Kunil, K. Kato, S. T. Kim, and I. Akasaki, "Room-temperature violet stimulated emission from optically pumped AlGaN/GaInN double heterostructure," *Appl. Phys. Lett.*, vol. 64, no. 11, pp. 1377–1379, 1994.

[64] I. Akasaki, H. Amano, S. Sota, H. Sakai, T. Tanaka, and M. Koike, "Stimulated emission by current injection from an AlGaN/GaN/InGaN quantum well device," *Jpn. J. Appl. Phys.*, vol. 34, no. 11B, pt. 2, pp. L1517–L1519, 1995.

[65] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyoku, "Optical gain and carrier lifetime of ingan multi-quantum well structure laser diodes," *Appl. Phys. Lett.*, vol. 69, no. 11, pp. 1568–1570, 1996.

[66] S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, "InGaN-based multi-quantum-well-structure laser diodes," *Jap. J. Appl. Phys.*, vol. 35, no. B, pt. 2, pp. L74–L76, 1996.

[67] M. Ueno, Y. Yoshizumi, Y. Enya, T. Kyono, M. Adachi, S. Takagi, S. Tokuyama, T. Sumitomo, K. Sumiyoshi, N. Saga, T. Ikegami, K. Katayama, and T. Nakamura, "InGaN-based true green laser diodes on novel semi-polar {20–21} GaN substrates," *J. Crystal Growth*, vol. 315, pp. 258–262, 2011.

[68] H. Yoshida, Y. Yamashita, M. Kuwabara, and H. Kan, "Demonstration of an ultraviolet 336 nm AlGaN multiple-quantum-well laser diode," *Appl. Phys. Lett.*, vol. 93, 2008, 241106.

[69] R. F. Kazarinov and R. A. Siris, "Possibility of amplification of electromagnetic waves in a semiconductor with a superlattice," (in Russian) *Fiz. Tech. Poluprov.*, vol. 5, no. 5, pp. 787–800, 1971.

[70] J. Faist, F. Capasso, D. L. Sivco, B. Sirtori, A. L. Hutchison, and A. Y. Cho, "Quantum cascade laser," *Science*, vol. 264, no. 5158, pp. 553–556, 1994.

[71] J. S. Roberts, R. P. Green, L. R. Wilson, E. A. Zibik, D. G. Revin, J. W. Cockburn, and R. J. Airey, "Quantum cascade lasers grown by metalorganic vapor phase epitaxy," *Appl. Phys. Lett.*, vol. 82, no. 24, pp. 4221–4223, 2003.

[72] R. P. Green, A. Krysa, J. S. Roberts, D. G. Revin, L. R. Wilson, E. A. Zibik, W. H. Ng, and J.W. Cockburn, "Room-temperature operation of InGaAs/AlInAs quantum cascade lasers grown by metalorganic vapor phase epitaxy," *Appl. Phys. Lett.*, vol. 83, no. 10, pp. 1921–1922, 2003.

[73] D. Bour, M. Troccli, F. Capasso, S. Corzine, A. Tandon, D. Mars, and G. Hofler, "Metalorganic vapor phase epitaxy of room-temperature low-threshold InGaAs/AlInAs quantum cascade lasers," *J. Crystal Growth*, vol. 272, pp. 536–530, 2004.

[74] J. Faist, private communication, May 2012.

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