Semiconductor Alloy Lasers—1962

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(Invited Paper)

Abstract—**Following the report of high-efficiency generation and transmission of recombination radiation from Zn-diffused GaAs p–n junctions at the 1962 IRE Solid State Device Research Conference (July, Durham, NH), a many-laboratory race began to construct a semiconductor laser. Although it is widely believed that only GaAs was involved in the research that led to a semiconductor laser, the visible-spectrum alloy $GaAs_{1-x}P_x$ was in the middle of this activity and was (fall of 1962), with GaAs, a first semiconductor laser, not to mention the first laser in a semiconductor alloy or crystal that could be "tuned" in energy gap (and wavelength) from direct-gap to indirect-gap. The ternary $GaAs_{1-x}P_x$ was the forerunner of all present-day III–V alloys used in heterojunction devices. The sequence of events leading to the $GaAs_{1-x}P_x$ laser, as well as its introduction in modified form as the first practical LED, are described.**

I. Introduction

BEFORE talking about semiconductor lasers, I think I should mention that at the end of World War II I studied vacuum tube electronics, including how a tetrode generates a negative resistance and why a thyratron switches. Negative resistance and switching have a bearing on what I will have to say later. I even tried my hand at microwave tube research, specifically electron-beam bunching with a multipactor. When John Bardeen came to Illinois (1951), however, I switched to learning about semiconductors and to working with Ge. After finishing a thesis under Bardeen's guidance, I went to work (1954) for John Moll at Bell Telephone Laboratories on switching devices. It did not take Moll much to convince me that we had to work on Si (for pnpn switches and for switching transistors), and that the "right" technology, which would have to be discovered and developed, was impurity diffusion, top-surface pattern definition, and metallization. We had our share of success with all of this, and I hope, elsewhere, to describe why I consider John Moll the prime instigator, after the transistor inventors, of today's Si chip technology.

After serving in the U.S. Army (1955–57), I went to General Electric (GE) in Syracuse, NY, and back to work on Si switching devices, in fact, on the SCR-version of the Si pnpn "thyratron" that our Bell Labs' work first introduced [1]. Incidentally, when I was in the U.S. Army in Japan, via John Bardeen's introduction, I met Makoto Kikuchi and George (Mitio) Hatoyama, and others, such as Leo Esaki. (Bell Labs did not object to me talking about our Si work as long as I protected oxide masking. Maybe Kikuchi and I in 1956 and 1957 first introduced Si technology in Japan as part of our Saturday seminars at Denki Shikenjo.)

I think I have made it obvious that when the Ge tunnel diode was first described by Esaki, I had more than enough background with switching, negative resistances, and Si to feel immediately that I could, and should, build Si tunnel diodes. I did, and after the 1959 Solid State Device Research Conference (Ithaca, NY) showed Rediker how Si tunnel diodes could be simply built. Vacuum tube negative resistances always seemed peculiar to me (somewhat artificial), and a tunnel diode was a more tangible, more obvious form of negative resistance. Apart from the fact that we observed the first inelastic tunneling (phonon-assisted tunneling) via liquid-He measurements on Si tunnel diodes [2], these devices did not prove to be very useful. They did usher in tunneling spectroscopy, however, which is now a standard research technique with an all but forgotten origin [3]. Because of the voltage limitations of Ge and Si tunnel diodes, it was natural to consider other materials, hence the III–V's. Very quickly we learned that GaAs tunnel diodes could be built [4], but were dismayed at how quickly they failed. But whether we realized it or not, we were on the road to something much more important.

At the IRE Solid State Device Research Conference (SSDRC) in 1960 in Pittsburgh, PA, John Marinace described the epitaxial growth of Ge on GaAs, which represented probably the world's first high-quality heterojunctions. I went home and decided that I could do the opposite, and that is grow, via closed-tube vapor phase epitaxy (VPE), GaAs on Ge. When I did this and showed the results to my Syracuse GE colleagues, they considered me crazy for even thinking that I could transport a multicomponent system and seed it epitaxially. By the end of 1960 in two Air Force Contract reports (AF 19(604)-6623, October 1960 and December 1960), with a large formal electronics industry mailing list, I described the vapor phase epitaxial (VPE) growth of GaAs on Ge, GaAs on GaAs, GaP on GaP, GaP on GaAs, and the VPE synthesis of $GaAs_{1-x}P_x$ (also the growth of $GaAs_{1-x}P_x$ on $GaAs_{1-y}P_y$). The reason that I did this initially was: 1) to have a new way to make a tunnel diode, a tunnel diode that I hoped would not fail, and 2) to make a higher band-gap material ($GaAs_{1-x}P_x$), and thus a higher voltage tunnel diode. I succeeded in making a VPE GaAs tunnel diode and the higher band-gap (red-gap) alloy which, with further processing, yielded $GaAs_{1-x}P_x$ tunnel diodes. Our

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first accounts of this work were in Air Force reports in 1960, the AIME Electronics Materials Conference in Los Angeles, CA, in August 1961, and then in the much delayed written meeting report (1962) [5]. Beyond tunnel diode interests, I realized that I had available to me a very general heterojunction technology [6], and because of the Air Force contract support, in late 1960 showed my results to two visitors, F. V. Williams and R. Ruehrwein (Monsanto), who immediately extended what I had done in a closed tube to open-tube technology [7].

II. 1962 Solid State Device Research Conference

In the period of time from the 1960 SSDRC to the 1962 SSDRC, which slipped into July in Durham, NH, I gained a lot of experience in III–V epitaxy and III–V device experiments, including on p–n junction light emitters. I even considered (1961) leaving GE to join Hewlett–Packard (HP) to help form Hewlett–Packard Associates (HPA) and build light emitters. I didn't leave GE and went to the 1962 SSDRC, not to deliver a paper on luminescence, but on double injection in semi-insulating GaAs and in deep-level doped Si [8] and, of course, to see friends and hear the work of others. I remember many interesting SSDRC's, but the one in 1962 was particularly memorable for many reasons. For example, I remember a friendly argument that Art D'Asaro and I waged with Bob Noyce on III–V versus Si device research. Noyce maintained that if we persisted in our interest in III–V's, he would push Si research further, well beyond us. He was right concerning Si, but was incorrect in assuming III–V's did not have much to offer.

I don't remember the junction luminescence reports at SSDRC (1962) of any group except that of Keyes and Quist [9] (Rediker's group, Lincoln Laboratory). I think the reason for this was the impressive nature of the Keyes and Quist report of GaAs p–n junction luminescence, its high efficiency, and the fact that GaAs junctions had already been used to transmit signals. Also, various Lincoln Laboratory friends explained informally to me how they entered this work, and even speculated that maybe all that a GaAs p–n junction required to operate in stimulated emission was low temperature and a high magnetic field to overcome the lack of discrete transitions. It is important to note that informal discussions of stimulated emission in GaAs were already a part of the 1962 SSDRC; at least they were for some of us. In other words, if GaAs was such a good spontaneous infrared (IR) light source, what more would be required to make it (a p–n junction!) coherent? Some people thought that rare earth dopants should be introduced into GaAs p–n junctions and would (mysteriously) establish discrete levels and laser transitions, e.g., akin to ruby, YAG, etc. Since I had already seen ruby lasers at GE, I knew what to expect of visible-spectrum coherent light, and to my SSDRC roommate I speculated that all that might be needed was to operate a p–n junction in an external cavity. I didn't like the idea of contaminating the crystal with deep levels. I steadily maintained this position later in further arguments with GE Electronics Laboratory (Syracuse) staff members, the ones who first showed me operating ruby lasers and considered themselves experienced with lasers. If there was any hope to operate a p–n junction laser, I was sure I was in the most advantageous position relative to others because I knew how to make red-spectrum $GaAs_{1-x}P_x$, and furthermore was experienced in making p–n junctions in III–V's, including in the high-gap alloy that most interested me.

To write of these matters so many years later based on just memory would be somewhat awkward, but fortunately many of my notes, correspondence, reports, etc., still exist. At this point I wish to quote part of a letter I wrote in 1966 to a GE patent attorney, Robert Mooney, concerning my diligence, or lack of diligence, in pursuing cleaving as a means to form a semiconductor laser cavity. My letter, an October 13, 1966, reply to questions from Mooney, says something also about how we made a visible-spectrum laser. After the first paragraph, the letter reads as follows.

> "Enough of generalities. Apparently the problem is to show reduction to practice. *In a certain sense* reduction to practice was never established in our work. It is futile for you to seek non-existent notebook entries. These statements require explaining. Also, in all this is some rather bitter irony; while I was trying to cleave Ga(AsP), I was losing position and time to the boys playing the easier GaAs game. Note: GaAs was a material that I could easily cleave, and I proved it to Hall on a wafer.
>
> But now back to the beginning:
>
> 1) After SSDRC, July, 1962, U of New Hampshire, many of us had "laser" on our minds.
>
> 2) I had external cavity on my mind in which to try a junction.
>
> 3) August, 1962 Hall and I talked about the problem. He told me he was already at work on a GaAs device and was going to build a cavity right onto the device by polishing, whereupon I suggested he should cleave. He preferred to polish. I sent him a cleaved GaAs wafer. (Tom Selig roomed with me at New Hampshire and will confirm some of my speculations on a possible semiconductor laser.)
>
> 4) For weeks dating from Aug, 1962 I tried to build a Ga(AsP) laser, on polycrystalline material. You will appreciate I could not easily find a cleavage plane on a crystallite in poly material. This cost us time, because you realize we could have polished a cavity.
>
> 5) I felt strongly enough about cleaving to send Hall a sample (GaAs) and I wrote the disclosure on cleaving dated Oct. 4, 1962 which you have, and of course I continued attempting to cleave.
>
> 6) With a G.E. study team L. Apker visited (check Company dates) and saw our Ga(AsP) "red" diodes. *Roy knew we were trying to cleave!*
>
> 7) Finally Hall was successful with GaAs and Apker called to tell me. (That was a surprise, because being in the "visible", I thought I'd be able to recognize, visually, a laser first. But Bob did it easily, i.e., recognize lasing in the IR, with instruments.)
>
> 8) Apker in his call pleaded that I give up trying to cleave and instead polish. He knew our junctions were good; he saw them. He realized I was having a tough problem trying to hit cleavage planes in poly wafers of Ga(AsP).
>
> 10) Finally I decided, Oh what the hell!, I'll polish up a batch (Oct 9), and indeed from lot #28 we immediately had "red" lasers, the first ever (and I'll bet "red" before IBM and Lincoln had Fabry–Perot IR GaAs lasers). Incidentally, we uncorked our own polishing scheme which did not at all resemble Hall's. You should realize, and it is recorded, the batch from

which we got Ga(AsP) lasers was on a crystal grown in September, 1962. And had we polished immediately, Hall's GaAs Laser would not have come any sooner than a Ga(AsP) laser from us. *Trying to cleave intractable poly material held us up*! Neither could we get a reduction to practice on cleaving, nor could we demonstrate a Ga(AsP) laser until we went to polishing. Recall there was no need for us just to duplicate what Hall was trying in GaAs, so we did not have the advantage of a simple system to cleave. But let me hasten to add that now that single crystal Ga(AsP) can be grown, we can and do cleave laser cavities. Also, let me remind you that patent 3,245,002 (G.E.) has claims on Ga(AsP), and that was our work, and at the time was more important to us than a continued attack on reducing cleaving to practice. It can not be refuted that we worked hard to cleave, but under impossible conditions. We can prove that our diligence in trying to cleave actually hurt us, held us up. Check with Roy Apker. He was the one who pleaded with me to give up cleaving and polish. Witnesses to all this were primarily Sam Bevacqua, and then Chet Bielan, Stan Lubowski, Fred Carranti, Bernie Hess, Leslie Alt (X-ray Dept now), and probably our secretary Doris.

Finally, let me say that I don't know who in G.E. finally used cleaving. Although I tried to sell G.E. cleaving, *and put it on paper*, cleaving cost me scientifically some measure of propaganda defeat at the hands of GaAs workers, because the idea of cleaving slowed up Ga(AsP) work. Apker and Hall can confirm this."

The letter I have quoted above slices very rapidly through much of what occurred from July (1962 SSDRC) through October 1962. Of course, that is not all. For example, I did not know that Hall had any contact with others who might have been thinking about stimulated emission in semiconductors. I did not know this until I saw Hall's 1976 paper [10] and his reference to discussions with M. Bernard [11]. Although the Bernard and Duraffourg paper [11] has its own importance, I don't consider this paper as key in the sequence of events leading to a semiconductor laser for at least two reasons. One is that it was the Keyes and Quist report that got our attention, and not anything else. Also, the type of Zn-impurity diffused GaAs diodes typical of the work of Rediker and coworkers [12] and the similar diffused p–n junctions we made in $GaAs_{1-x}P_x$ (for light-emitting diodes) were doped degenerately on both the substrate side (n) and on the Zn-diffused side (p). The doping levels were easily high enough for degeneracy, particularly at the low temperatures (77 K) that we typically employed for tests on p–n junctions.

I might mention that low temperature diode operation was something that we regarded as quite routine after our tunnel diode work [2]. For example, to show Apker when he visited (September 1962) how bright our $GaAs_{1-x}P_x$ p–n junctions were, I "froze" them in liquid N_2 to low temperature and then, with current flowing, removed them from the dewar for viewing. They were a dazzling red and impressive. Before November 1, I also performed this demonstration for Rediker's benefit on the occasion of a late-evening Syracuse-area IRE seminar held at Electronics Park (GE). This made it convenient for me to take Rediker into our laboratory, along with some stragglers from the seminar. I remember posing a question something like: "What do you think it will require to make a semiconductor laser? Afterall, look how bright these diodes are!" What I didn't realize then was that Rediker already knew that GE was operating semiconductor lasers. I found this out later (November 1, 1962) when Rediker sent me a note, attached to a copy of the Lincoln Laboratory laser manuscript [13], that read, "It was a lot of fun acting dumb in Syracuse with you." (At the time we weren't telling others about semiconductor lasers, not even others in GE, and did play "dumb.")

Whether we realized it or not at the time, carrier injection for this form of p–n junction is inevitably all electron injection into the p-type side. In other words, the significant diffused-impurity (acceptor) gradient and the effect of the donor compensation on the p-type side of the junction (not to mention the high electron mobility) insure 100 percent electron injection, with excellent confinement of excess carriers near the junction. The injected carriers in such a junction, all on one side, simply do not spread out before recombining, and are easily driven to degenerate levels at low temperatures and large currents. The issue of carrier inversion and how to achieve it was solved by the crystal, not the cleverness of design (or by even much consideration of the problem). Others might say that there were important papers that led us to the semiconductor laser; I dispute this. The only theoretical paper that might have mattered is the von Neumann paper [14], had we known about it. But it also did not matter except now to indicate how early and how advanced were von Neumann's ideas, and to show, in comparison, how nebulous were other notions of semiconductor lasers.

III. The $GaAs_{1-x}P_x$ Laser

The portion of the 1966 letter to Mooney I quoted above already outlines how we arrived at a $GaAs_{1-x}P_x$ p–n junction laser. I wish to add a few details. As described elsewhere [5], to synthesize $GaAs_{1-x}P_x$ we simultaneously transported GaAs and GaP in a quartz ampoule with $PbCl_2$ or PbI_2 supplying the halogen transport agent; a donor such as Se or Te was also included in the ampoule to dope the crystal. The lead (Pb), which is more or less insoluble in $GaAs_{1-x}P_x$, deposited on the crystal at the end of the transport process and did not create any problems. If the $GaAs_{1-x}P_x$ synthesis process, which is a VPE process [5], is carried out slowly enough, it is possible to grow a single crystal such as that shown in Fig. 1. Generally we were impatient and grew a one or two gram crystal in a couple of days, frequently over a weekend. In this case the crystal seeded at multiple sites at the cooler end of the ampoule, and we grew relatively rapidly a rather large poly-crystal with crystallites that were much larger than typical device dimensions. After slicing the crystal into wafers, and polishing and etching the wafers, we diffused Zn into them (with as usual, an As overpressure) to a depth $\sim 25\ \mu m$, and then etched or polished off the back-side p-type region. As already mentioned, I tried unsuccessfully to cleave these wafers to form reflecting edges. My notions of how to cleave are shown in the disclosure of Fig. 2, which is dated October 4, 1962, and also mentions that I talked with Hall on August 31, 1962. (Actually, because of an Air Force Contract that we shared, I visited and talked with Hall on August 29, 1962).

When Apker called me in late September or early Oc-

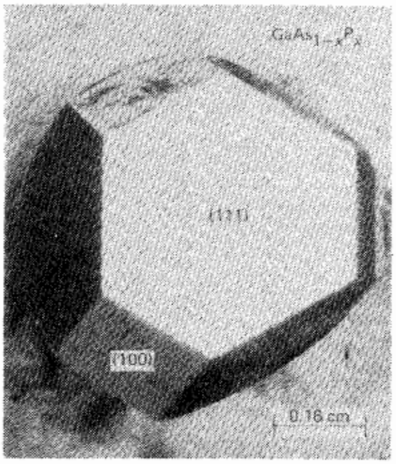
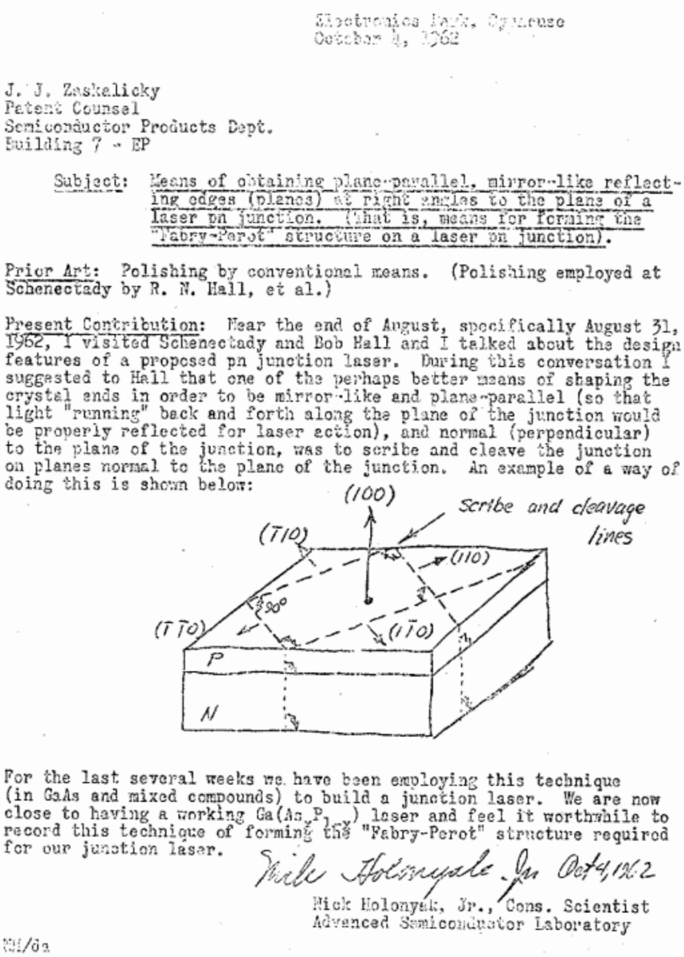


Fig. 1. Single crystal $GaAs_{1-x}P_x$ crystal grown via vapor phase epitaxy (VPE), in a closed quartz ampoule, showing well-developed low index {111} and {100} natural facets.



Electronics Park, Syracuse
October 4, 1962

J. J. Zaskalicky
Patent Counsel
Semiconductor Products Dept.
Building 7 - EP

Subject: Means of obtaining plane-parallel, mirror-like reflecting edges (planes) at right angles to the plane of a laser pn junction. (That is, means for forming the "Fabry-Perot" structure on a laser pn junction).

Prior Art: Polishing by conventional means. (Polishing employed at Schenectady by R. N. Hall, et al.)

Present Contribution: Near the end of August, specifically August 31, 1962, I visited Schenectady and Bob Hall and I talked about the design features of a proposed pn junction laser. During this conversation I suggested to Hall that one of the perhaps better means of shaping the crystal ends in order to be mirror-like and plane-parallel (so that light "running" back and forth along the plane of the junction would be properly reflected for laser action), and normal (perpendicular) to the plane of the junction, was to scribe and cleave the junction on planes normal to the plane of the junction. An example of a way of doing this is shown below:

For the last several weeks we have been employing this technique (in GaAs and mixed compounds) to build a junction laser. We are now close to having a working $Ga(As_xP_{1-x})$ laser and feel it worthwhile to record this technique of forming the "Fabry-Perot" structure required for our junction laser.

Nick Holonyak Jr Oct 4, 1962

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NH/da

Fig. 2. Disclosure submitted to GE patent counsel on October 4, 1962, showing how to cleave and form a semiconductor laser cavity. A correction to this disclosure (not shown) indicates that this idea was discussed with R. N. Hall in Schenectady, NY, on Aug. 29, 1962.

tober (1962) to tell me that Hall and his co-workers were successful in operating a GaAs laser, he argued again (but now I had to agree) that I give-up cleaving and polish mirrors on my $GaAs_{1-x}P_x$ diodes. To accomplish this I first put black wax threads parallel across a Zn-diffused

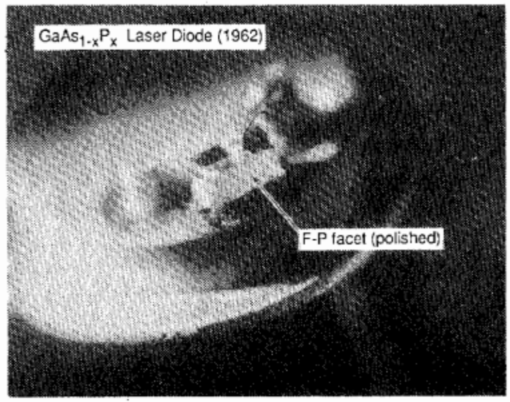


Fig. 3. Polished Fabry–Perot (F–P) mirror facet of a $GaAs_{1-x}P_x$ diode laser (Zn-diffused p–n junction, VPE n-type crystal) attached via a soft alloy between the two contact leads of a TO-18 header. An etched p-type mesa at the top of the crystal is contacted via another soft alloy to an annealed Ni lead.

wafer and carefully melted the wax into half cylinders on the crystal. This served as a mask against deep etching, which we took through the diffused p-type region down into the n-type substrate. We then waxed the wafer to a glass plate and took deep parallel saw cuts (well into the glass plate) at right angles to the long stripe-etched p-type diffused mesas. This resulted in narrow strips with saw-cut sides but with good parallelism, and, of course, with many etched p-type mesas across the strips. My trick for polishing the Fabry–Perot mirrors was to take these strips and wax them, on the saw cut faces, at random all around on a small glass disc. Then I polished the opposite saw-cut faces in several stages and finished the polishing with alumina on a polishing plate that I made by loading epoxy with an alumina filler. I thus avoided rounding of the edges by using a relatively hard plate (but one easy to grind flat). I turned the diffused strips over and repeated the process to form the second set of mirrors. We scribed and cleaved the broad stripe mesas apart and then alloyed them to headers, as shown in the photograph of Fig. 3. This photograph shows one of the polished mirror faces and, although it is not too evident, a mesa on top (center) with a Ni lead attached to it. We generally didn't bother to metallize the wafer because I had good-wetting home-made Pb + In + Ag + Te (85 + 10 + 2.5 + 2.5 percent) and Pb + In + Ag + Zn (85 + 10 + 2.5 + 2.5 percent) alloys to attach the dies to headers and to attach an annealed Ni lead to the diode mesa, as in Fig. 3.

We assembled our first lot of polished-cavity $GaAs_{1-x}P_x$ lasers on Tuesday, October 9, 1962. Now that at last I had a group of diodes with Fabry–Perot mirrors, I decided that it would be quicker to check our diodes for stimulated emission in Schenectady, NY, where Hall's group already had in place all the necessary apparatus. On October 10, 1962, on the diode shown in Fig. 4, we took the $GaAs_{1-x}P_x$ laser data reported in the paper that I published with Bevacqua [15]. In my notebook in Syracuse the next day (October 11, 1962) I wrote (Fig. 5) as follows.

"Yesterday, at Schenectady, we tried diode # (diffusion run 28) which we assembled here into a plane parallel structure on Tues., Oct 9, 1962

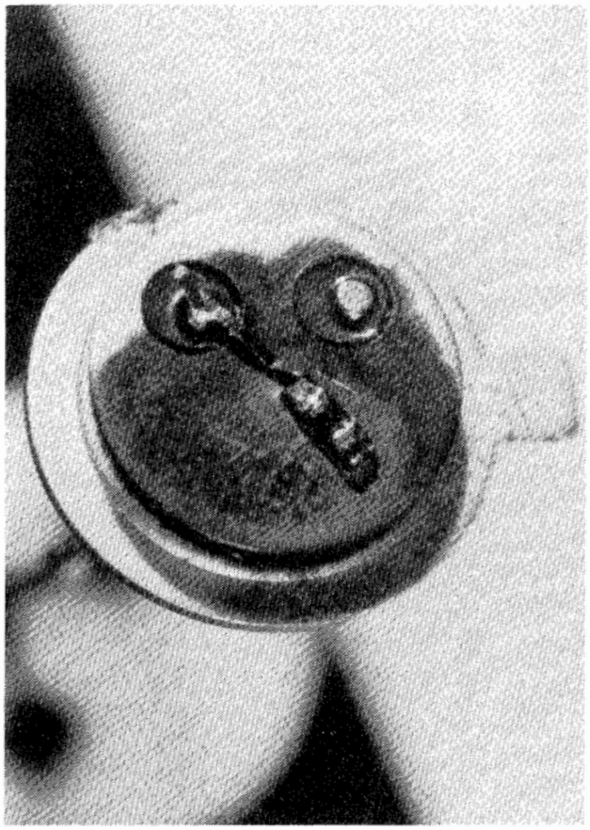
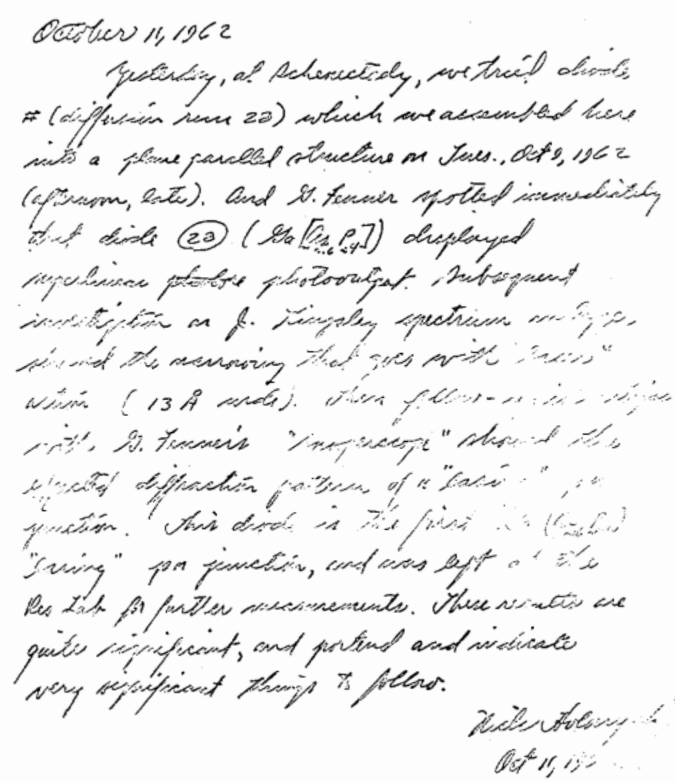


Fig. 4. First visible-spectrum $GaAs_{1-x}P_x$ diode laser. The p–n diode is assembled on a TO-18 header (GE, Syracuse, NY, Oct. 9, 1962). (See text and Fig. 5).



October 11, 1962

Yesterday, at Schenectady, we tried diode # (diffusion run 22) which we assembled here into a plane parallel structure on Tues., Oct 9, 1962 (afternoon, late). And G. Fenner spotted immediately that diode (28) (Ga[$As_{1-x}P_x$]) displayed superlinear ~~photo~~ photooutput. Subsequent investigation on J. Kingsley spectrum analyzer showed the narrowing that goes with "laser" action (13 Å wide). Then follow-up investigation with G. Fenner's "snooperscope" showed the expected diffraction pattern of a "lasing" pn junction. This diode is the first Ga($As_{.6}P_{.4}$) "lasing" pn junction, and was left at the Res Lab for further measurements. These results are quite significant, and portend and indicate very significant things to follow.

Nick Holonyak Jr.
Oct 11, 19[illegible]

Fig. 5. Notebook entry (GE, Syracuse, NY, October 11, 1962) concerning the laser operation of the p–n $GaAs_{1-x}P_x$ diode laser of Fig. 4. (See text and [15]).

(afternoon, late). And G. Fenner spotted immediately that diode 28 (Ga[$As_{1-x}P_x$]) displayed superlinear photooutput. Subsequent investigation on J. Kingsley spectrum analyzer showed the narrowing that goes with "laser" action (13 Å wide). Then follow-up investigation with G. Fenner's "snooperscope" showed the expected diffraction pattern of a "lasing" pn junction. This diode is the first Ga($As_{\sim.6}P_{\sim.4}$) "lasing" pn junction, and was left at the Res Lab for further measurements. These results are quite significant, and portend and indicate very significant things to follow."

I was, of course, elated to see that my polished-cavity $GaAs_{1-x}P_x$ diodes were lasers, but I was also mildly disappointed because Hall had clearly won the race that began at SSDRC to achieve stimulated emission in a semiconductor. I didn't feel too bad about that, however, because his notion that the semiconductor "slab" itself could serve as the laser cavity was better than my idea of operating a p–n junction in an external cavity. (External cavity semiconductor laser operation did become important later, particularly in external grating tuning.)

Before I left Schenectady on October 10 to drive back to Syracuse, Hall invited me to have dinner with him and his family and urged me to quickly prepare a paper for publication. In view of the fact that Hall already was operating GaAs lasers and had submitted a paper to *Physical Review Letters* [16], I considered the race over and didn't feel there was any need for speed in reporting the laser operation of $GaAs_{1-x}P_x$. Because of what the world was doing, that thought was a mistake. In fact, had I polished Fabry–Perot mirrors on our diodes any sooner, in September as I could have, our paper would easily have made the November issue of *Applied Physics Letters*, and not the December issue. From "inside" information on the operation of *Appl. Phys. Lett.*, Apker told me later that it would have helped if I hadn't waited until the following week to ship my paper. In any case, little did I realize how much publicity would be attached to semiconductor lasers, and that in December the great New York newspaper strike would occur. As it happened, GaAs received (November) the full publicity treatment, and $GaAs_{1-x}P_x$ was all but forgotten, as though it was not a *first* semiconductor laser. It was.

IV. III–V Semiconductor Alloys

I think I have made it clear that our $GaAs_{1-x}P_x$ lasers were not spin-offs from GaAs lasers. In fact, I fully intended to win the race (started at SSDRC) to a semiconductor laser by deliberately working in the visible. The fact that we had to make our crystal, compared to the much simpler problem of working with a shelf-item crystal (GaAs), of course, cost us time. However, my experience in working with $GaAs_{1-x}P_x$ for two years (1960–1962) could not be easily duplicated by others, and for a considerable time we held a monopoly on this area of work. For a year or so we represented (i.e., our experimental units were) the entire available supply of $GaAs_{1-x}P_x$ lasers, including the commercial units first offered for sale (December 1962) by GE for \$2600 apiece. These were, in fact, made in our laboratory (Syracuse). Later (1965) Allied Radio Corporation (Chicago, IL) offered our laser diodes (#H1B1) for sale at half this price [17]. Incidentally, since Texas Instruments offered GaAs infrared emitters (incoherent) for \$130, someone in GE (1962) thought a GaAs laser was worth \$1300 and a $GaAs_{1-x}P_x$ laser (visible) even more, \$2600.

In late 1962, well after our paper was submitted to *Appl. Phys. Lett.*, but before it was published, I was lucky enough to receive (from a Department of Defense source) another group's contract report that read as follows.

> "The discovery of lasing action in GaAs diodes doped with ordinary donors and acceptors has led to a re-evaluation of our previous emphasis on rare earth and transition metal impurities. Without entirely abandoning the previous approach, we are emphasizing extension of the spectral region of injection lasers by attempts to obtain lasing action in new materials."

A little later the report read:

> "We have also begun to explore the system GaAs–GaP as a suitable laser material because of the possibility of producing emission in the visible range of the spectrum. Our first attempt consisted in trying to make a 20% GaP alloy by diffusing phosphorus into GaAs wafers. The diffusion was carried out over a weekend at 1200°C (m.p. of GaAs: 1240°C). . . ."

I realized immediately that this was a poor way to try to make $GaAs_{1-x}P_x$ and was doomed to failure. Another report in this sequence two months later indicated further failure in work with the alloy. Also, here was another group thinking in terms of "rare earth and transition metal impurities" (why?). By the time our $GaAs_{1-x}P_x$ laser paper was published [15], I knew directly, and from what I had learned of other people's work, that no one else's notions of semiconductor lasers, except Hall's idea to make the cavity integral with the crystal, exceeded my own ideas. Our laser diodes were the first that could be seen by their own light and be photographed (see [18, p. 35]), and because of the diffraction pattern we could see directly on a ground-glass screen, and because of the obvious laser speckle, I knew I was justified in my original idea (dating to SSDRC 1962 and the Lincoln Laboratory report) to build a visible-spectrum $GaAs_{1-x}P_x$ laser. We could simply look at our lasers and see that they were lasers.

Not only was $GaAs_{1-x}P_x$ in the running to become the first semiconductor laser, the alloy, indeed, represented something more general. For some reason this was overlooked by others [19]. Before our visible-spectrum semiconductor laser operation, which *required* a III–V alloy, it was not known how serious alloy disorder might be. Our data showed convincingly that alloy disorder was not intrinsically a problem and that virtual crystal models for the energy band behavior made sense [20]. We established the fact that crystal composition could be used to "tune" energy gaps and the wavelength of laser operation, and very quickly we ran into the limitations of the direct–indirect crossover [21]. Subsequent high pressure measurements on our $GaAs_{1-x}P_x$ lasers by others confirmed our composition-tuning results, and the fact that the crossover from direct-gap to indirect-gap cuts-off laser operation. These results made apparent how weak the proposals were to make, for example, Ge lasers, not to mention operate them normal to the junction plane. Above all, we showed that semiconductor alloys had a place in practical device electronics. In fact, without semiconductor alloys the entire present-day field of III–V heterostructure electronics, including quantum well and superlattice electronics, would not exist. There is no doubt that it was $GaAs_{1-x}P_x$ lasers that proved the worth of III–V alloys.

Several more events occurred in late 1962 that are pertinent to semiconductor laser history and should be mentioned. In October 1962 (between the 11th and 23rd) John Bardeen called asking me to give a seminar, and, in spite of GE's secrecy in this area, I revealed our laser work to Bardeen and promised to give a seminar on semiconductor lasers as soon as GE released the work. In our telephone conversation Bardeen made the surprising comment that John von Neumann first considered the idea of semiconductor lasers in 1953. On October 23, 1962, I received from Bardeen a handwritten letter and a copy of his typewritten summary of von Neumann's manuscript, the summary which later was published [14]. In his letter, after some comments about von Neumann's work, Bardeen also wrote as follows.

> "We thought about trying to make a laser here operating on this principle some two or three years ago, but couldn't find a material with a sufficiently high efficiency for recombination radiation."

When I gave the promised semiconductor laser seminar in Urbana in November or December (1962), Bardeen showed me von Neumann's manuscript [14], and in 1965 gave me a copy that I have on occasion shown to others to settle arguments concerning the so-called invention of the semiconductor laser. It is obvious that the idea of a semiconductor laser was not unique when we first constructed it in 1962. It is also obvious that all of the papers written on the possibility of a semiconductor laser, papers written before the fall of 1962, had nothing to do with the construction of a semiconductor laser, which was inevitable after SSDRC (July 1962). What mattered in making a semiconductor laser was what was happening in semiconductor device research, not laser research as such.

There are further items dealing with semiconductor laser history dating back to 1962 that are worth recalling. Because of the depth to which GE had advanced in this area of work by the fall of 1962, a conference was held in Schenectady on November 28, 1962, to which, to the best of my recollection, only members of the Department of Defense were invited. This meeting, "Symposium on Semiconductor Lasers," which was also the title of the printed compilation given the participants, was probably the first conference ever on semiconductor lasers. Hall and his co-workers were the morning speakers and talked about GaAs lasers. In the afternoon session I described visible-spectrum $GaAs_{1-x}P_x$ lasers.

One more person outside of GE who saw our laser work was John Bardeen, who stopped briefly in Syracuse on a Saturday in late November or early December (1962) while on his way back to Urbana from an East Coast meeting. I invited some local GE managers to meet Bardeen and to see the same semiconductor laser demonstration we had hurriedly planned for him. Les Alt, a GE Syracuse colleague, helped me cool (77 K) the laser diode(s), and we monitored the input current pulse on the upper trace of a dual-trace oscilloscope and the light output on the lower trace, with the two amplifiers set to give equal deflection on both traces at low level. With increasing current the bottom trace abruptly cut through and exceeded the upper trace. This baffled my local colleagues who knew little about stimulated emission. They immediately asked questions, and Bardeen quietly explained what we had just observed on the oscilloscope. This was the first time he, as well as our local guests, had seen an operating semiconductor laser. Nevertheless, it was obvious that he already knew in some depth what to expect of stimulated emission. It is clear the idea was not new to him.

V. From Lasers to LED's

I have already mentioned that in our work with $GaAs_{1-x}P_x$, and the "tuning" of its composition (x), we very quickly ran into the limitations of the crossover from a direct-gap to an indirect-gap crystal (i.e., $x \equiv x_c \approx 0.45$) [21]. Near the direct–indirect crossover ($x \lesssim x_c$) our diodes were extremely bright, particularly when viewed cold (77 K). On one lot of this material, for contact reasons we attached a small metal tab on the substrate side (n-type) of each diode and alloyed a small Pb + In + Ag + Zn (85 + 10 + 2.5 + 2.5 percent) ball on the Zn-diffused (p-type) top side, and then (in the Syracuse Bldg. 7 Si-diode operation) we dropped many of these $GaAs_{1-x}P_x$ p–n junctions into little commercial cylindrical glass packages that had a contact lead on one end and an S-spring contact lead that could be sealed-in on the other end. These were probably the first ever *packaged visible-spectrum* $GaAs_{1-x}P_x$ light emitting diodes (LED's). At the Schenectady semiconductor laser conference (November 28, 1962) these were the most convenient devices for me to demonstrate in order to show the light-emitting capabilities of $GaAs_{1-x}P_x$. These were convenient items to also give away and, although some of our early $GaAs_{1-x}P_x$ lasers still exist, all of these early LED's vanished.

The demonstration of semiconductor lasers in 1962 was a very exciting development. It confirmed an important idea, the possibility of stimulated emission (and laser oscillation) in a semiconductor. As practical devices, however, the first semiconductor lasers were sorely lacking. On the other hand, our LED's were immediately practical, and I volunteered this judgment to a *Reader's Digest* editor, Harlan Manchester, who had heard of our visible-spectrum laser work and called to ask about it [22]. Manchester quotes me as having said:

"We believe there is a strong possibility of developing the laser as a practical light source." . . . "Much more experimental work must be done, and it might be ten years or more before such a lamp could be ready for wide use. However, within a year we should have them ready for computer indicators and many other electronic devices, where they should be very useful because of the small size, and speed of action."

My optimistic comment to Manchester shows how good I considered our $GaAs_{1-x}P_x$ LED's to be, and how significant I considered the demonstration of stimulated emission in establishing, in the visible spectrum, the light-emitting properties of a semiconductor. I think only Rediker and I in 1962 believed there was much connection between stimulated emission and what constituted the basis for a good LED. There is no doubt that by the end of 1962, the laser operation of $GaAs_{1-x}P_x$ put the alloy well out in front of all other materials as an LED, except that the time scale for widespread general use (calculators, watches, instruments, etc.) was much longer than what I told Manchester. There is a lesson in all of this: development does not proceed as easily or as quickly or as cheaply as we might believe or wish. It takes a lot of commitment, both of time and effort. This is a hard lesson to learn, particularly for impatient managers.

Acknowledgments

I wish to mention that before I came to GE (1957), and a very productive association with Bob Hall on a number of problems, I was fortunate to have come under the influence of two men whom I especially wish to thank. The first is John Bardeen, who was my teacher and who for many years has been my friend and colleague, and a valued source of advice. The second is John Moll, who introduced me to Si device research. Both of these men have an unusual ability to see and to focus on what matters. For specifically supporting my early involvement with III–V compounds (tunnel diodes, lasers, LED's), I wish to thank a GE Rectifier Department manager, Ray York, and the Air Force (Cambridge). I was able to help York on SCR (thyristor) problems and he had the confidence to support my work on III–V's. Air Force Cambridge people also helped support my work on switching and negative resistance devices, and that led me into work on III–V compounds. Charlie Ryan, Dick Cornelisen, and their associates (Air Force, Cambridge) encouraged and supported my interest in III–V's when this was not popular work in Syracuse. I would not have been able to work on III–V's without the help of Ray York, Charlie Ryan, and Dick Cornelisen, and I want to take this opportunity to thank them. Also, I wish to thank a generation of doctoral students who have helped me learn more about III–V semiconductors and lasers. Finally, I want to mention Russell Dupuis, as well as Robert Burnham, and Gregory Stillman, for encouraging me to prepare this account, and R. T. Gladin, R. W. Kaliski, and B. L. Payne for help with the figures and manuscript.

References

[1] J. L. Moll, M. Tanenbaum, J. M. Goldey, and N. Holonyak, Jr., "PNPN transistor switches," *Proc. IRE*, vol. 44, pp. 1174–1182, Sept. 1956.

[2] N. Holonyak, Jr., I. A. Lesk, R. N. Hall, J. J. Tiemann, and H. Ehrenreich, "Direct observations of phonons during tunneling in narrow junction diodes," *Phys. Rev. Lett.*, vol. 3, pp. 167–168, 15 Aug. 1959.

[3] C. J. Adkins and W. A. Phillips, "Inelastic electron tunnelling spec-

troscopy," *J. Phys. C: Solid State Phys.*, vol. 18, pp. 1313-1346, March 10, 1985.

[4] N. Holonyak, Jr. and I. A. Lesk, "Gallium arsenide tunnel diodes," *Proc. IRE*, vol. 48, pp. 1405-1409, Aug. 1960.

[5] N. Holonyak, Jr., D. C. Jillson, and S. F. Bevacqua, "Halogen vapor transport and growth of expitaxial layers of intermetallic compounds and compound mixtures," in *Metallurgy of Semiconductor Materials, Vol. 15*, J. B. Schoeder, Ed. New York: Interscience, 1962 (AIME Conf., Los Angeles, CA, Aug. 1961), pp. 49-59.

[6] N. Holonyak, Jr., "Use of metallic halide as a carrier gas in the vapor deposition of III-V compounds," U.S. Patent No. 3 249 473, filed May 21, 1965 (Continuation of Applicat. 134 903, Aug. 30, 1961).

[7] R. Ruehrwein, "Use of hydrogen halide and hydrogen in separate streams as carrier gases in vapor deposition of III-V compounds," U.S. Patent No. 3 218 205, Nov. 16, 1965.

[8] N. Holonyak, Jr., S. W. Ing, Jr., R. C. Thomas, and S. F. Bevacqua, "Double injection with negative resistance in semi-insulators," *Phys. Rev. Lett.*, vol. 8, pp. 426-428, June 1, 1962; see also, N. Holonyak, Jr., "Double injection diodes and related DI phenomena in semiconductors," *Proc. IRE*, vol. 50, pp. 2421-2428, Dec. 1962.

[9] R. J. Keyes and T. M. Quist, presented at 1962 IRE Solid State Device Research Conference, Durham, NH (unpublished). see also, ——, "Recombination radiation emitted by gallium arsenide," *Proc. IRE*, vol. 50, pp. 1822-1823, Aug. 1962.

[10] R. N. Hall, "Injection lasers," *IEEE Trans. Electron Dev.*, vol. ED-23, pp. 700-704, July 1976.

[11] M. G. A. Bernard and G. Duraffourg, "Laser conditions in semiconductors," *Phys. Stat. Sol.*, vol. 1, no. 7, pp. 699-703, 1961.

[12] J. Lowen and R. H. Rediker, "Gallium-arsenide diffused diodes," *J. Electrochem. Soc.*, vol. 107, pp. 26-29, Jan. 1960; see also, J. Halpern and R. H. Rediker, "Low reverse leakage gallium-arsenide diodes," *Proc. IRE*, vol. 48, pp. 1780-1781, Oct. 1960.

[13] T. M. Quist, R. H. Rediker, R. J. Keyes, W. E. Krag, B. Lax, A. L. McWhorter, and H. J. Zeiger, "Semiconductor maser of GaAs," *Appl. Phys. Lett.*, vol. 1, pp. 91-92, Dec. 1, 1962.

[14] J. von Neumann, "Notes on the photon-disequilibrium-amplification scheme." See also, *John von Neumann: Collected Works, Vol. V*, A. H. Taub, Ed., summary by J. Bardeen. New York: Pergamon, 1963, p. 420. In addition, see J. von Neumann, "Notes on the photon-disequilibrium-amplification scheme (JvN), September 16, 1953," this issue, pp. 659-673; and R. D. Dupuis, "An introduction to the development of the semiconductor laser," this issue, pp. 651-657.

[15] N. Holonyak, Jr. and S. F. Bevacqua, "Coherent (visible) light emission from $Ga(As_{1-x}P_x)$ junctions," *Appl. Phys. Lett.*, vol. 1, pp. 82-83, Dec. 1, 1962.

[16] R. N. Hall, G. E. Fenner, J. D. Kingsley, T. J. Soltys, and R. O. Carlson, "Coherent light emission from GaAs junctions," *Phys. Rev. Lett.*, vol. 9, pp. 366-368, Nov. 1962.

[17] Allied Industrial Electronics Cat., no. 650, Chicago, IL, 1965, p. 77.

[18] A. L. Schawlow, "Advances in optical masers," *Scient. Amer.*, vol. 209, pp. 34-45, July 1963.

[19] N. Holonyak, Jr., "Laser action in $Ga(As_{1-x}P_x)$ and GaAs," *Proc. IEEE*, vol. 52, p. 104, Jan. 1964.

[20] H. Ehrenreich, "Band structure and transport properties of some 3-5 compounds," *J. Appl. Phys.*, vol. 32, pp. 2155-2166, Oct. 1961.

[21] N. Holonyak, Jr., S. F. Bevacqua, C. V. Bielan, and S. J. Lubowski, "The "Direct-indirect" transition in $Ga(As_{1-x}P_x)$ p-n junctions," *Appl. Phys. Lett.*, vol. 3, pp. 47-49, Aug. 1, 1963.

[22] H. Manchester, "Light of hope—Or terror?" *Readers Dig.*, vol. 82, no. 490, pp. 97-100, Feb. 1963.

Nick Holonyak, Jr. (S'51-M'59-SM'62-F'67) was born in the coal-mining town of Zeigler, IL, in 1928. He attended the University of Illinois, Urbana and received the B.S. (1950), M.S. (1951), and Ph.D. (1954) degrees, all in electrical engineering. A Texas Instruments Fellow in Semiconductor Physics (1953-1954) at the University of Illinois, he did his graduate work under the direction of John Bardeen.

He later was employed as a member of Technical Staff at Bell Telephone Laboratories (1954-1955) and helped demonstrate feasibility of the first diffused-impurity silicon devices, including transistors, p-n-p-n switches and SCR's. He served with the U.S. Army Signal Corps (1955-1957) at Ft. Monmouth, NJ, and at Isogo-ku, Yokohama, Japan. In 1957 he joined the Advanced Semiconductor Laboratory of the General Electric Company, Syracuse, NY and was successively employed (1957-1963) as a physicist, unit manager, and manager of the Advanced Semiconductor Laboratory, where he made contributions in the areas of power and signal p-n-p-n devices (including the invention of the shorted-emitter and symmetrical SCR and thyristor switches—TRIAC's, etc.), tunnel diodes, phonon-assisted tunneling, halide transport, and epitaxial growth of intermetallic compounds and compound mixtures (1960-1963), double injection and deep-impurity-level effects, junction luminescence (GaAsP LED's), and alloy semiconductor lasers (visible spectrum, GaAsP, 1962). His work from 1960 to 1962 on GaAsP and the construction in 1960 of a p-n junction in this crystal system, and a laser in 1962, led to the commercial introduction of GaAsP LED's, the first practical light emitting diode. Since 1963 he has been a Professor with the Department of Electrical and Computer Engineering and Materials Research Laboratory, University of Illinois, and is a member of the University of Illinois Center for Advanced Study. He and his doctoral students have worked primarily on III-V semiconductors, III-V alloy crystal growth and demonstration of red-orange-yellow-green stimulated emission in $In_{1-x}Ga_xP$, $In_{1-x}Ga_xP_{1-z}As_z$ and $Al_xGa_{1-x}As_{1-y}P_y$, stimulated emission on nitrogen trap transitions in the alloys $GaAs_{1-x}P_x$ and $In_{1-x}Ga_xP$, and heterojunctions in various ternary III-V's and in the quaternaries $Al_xGa_{1-x}As_{1-y}P_y$ and $In_{1-x}Ga_xP_{1-z}As_z$. His research since 1976 has been concerned with quantum-well light emitters and lasers, and with impurity-induced layer disordering, which selectively shifts lower gap quantum well layers to higher gap bulk layers. He is coauthor of the book *Semiconductor Controlled Rectifiers* (Prentice-Hall, Inc., 1964), editor of the Prentice-Hall series "Solid State Physical Electronics," has served on the Editorial Board of the *Proceedings of the IEEE* (1966-1974), *Solid-State Electronics* (1970-present), and the *Journal of Applied Physics* and *Applied Physics Letters* (1978-1980), and is a member of the Board of Editorial Associates of *Semiconductors and Insulators*.

Dr. Holonyak received a General Electric Cordiner Award (1962), and for his contributions to the field of visible light-emitting diodes and diode lasers, he was the recipient of the IEEE Morris N. Liebmann Award (1973) and the 1975 John Scott Medal (City of Philadelphia), the 1976 GaAs Symposium Award with Welker Medal, the IEEE Jack A. Morton Award (1981), and the Electrochemical Society Solid State Science and Technology Award (1983). He is a member of the National Academy of Engineering (1973), the National Academy of Sciences (1984), is a Fellow of the American Academy of Arts and Sciences (1984), and the American Physical Society, and has served on various IEEE, AIP, APS, and NAS committees.