Impurity-Induced Layer Disordering of Quantum-Well Heterostructures: Discovery and Prospects

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(Invited Paper)

***Abstract*—The circumstances leading to the discovery in 1980 of impurity-induced layer disordering (IILD) of AlAs–GaAs ($Al_xGa_{1-x}As$) quantum-well heterostructures (QWH's) and superlattices (SL's) are described. In view of the great stability of a QWH or SL (AlAs–GaAs) against ordinary thermal annealing, IILD came as a surprise, i.e., the lower temperature (selective) change from red-gap QW crystal to yellow-gap bulk crystal. Layer disordering can be carried out most effectively, via diffusion or implantation, with two-site dopants such as Zn (acceptor) or Si (donor), but is not restricted to active impurities alone. This maskable planar technology, which (with crystal conservation) transforms a coarser layered III–V "alloy" to a smoother stochastic alloy, and higher bandgap, is capable of forming, as desired, regions that confine carriers and photons. Accordingly, IILD has broad and growing use in optoelectronics (lasers, waveguides, etc.), particularly for III–V systems employing Al and Ga which easily substitute for one another and are sensitive to IILD. The atomic rearrangement of diffusion, a small scale (microscopic) lattice change, is in essence "amplified" by IILD into a large scale (macroscopic) layer change (patterned) that provides a method to study III–V diffusion mechanisms. IILD, a planar technology and growing area of work, is useful in optoelectronics applications as well as for basic diffusion studies in III–V's and potentially other crystal systems.**

***Index Terms*— Bulk-crystal larger bandgap, carrier confinement, disorder-defined lasers, disorder-defined optoelectronic devices, disorder-defined waveguides, impurity-free disordering, impurity induced layer disordering, layer disordering, layer interdiffusion, layer intermixing, layered alloy, photon confinement, quantum-well heterostructures, quantum-well smaller bandgap, stochastic alloy, superlattices, vacancy disordering.**

I. Introduction

DIFFUSION in semiconductors (carriers, impurities, lattice atoms) is a classic subject as well as experimental activity, which I was first fortunate to witness in J. Bardeen's laboratory (Urbana, IL, 1952–1954) when H. Letaw and L. Slifkin studied self-diffusion of radioactive Ge into Ge. These studies were part of Bardeen's long interest in diffusion and his concern with Ge. This was my first acquaintance with the concept of the thermally driven motion and rearrangement of crystal lattice atoms. Clearly atoms (Ge) do not necessarily just diffuse (self-diffuse) into a crystal (Ge); they rearrange the crystal. But how far into a crystal and to what extent, and how can this be observed? Ultimately of greater interest and importance was impurity diffusion in Si, which left behind Ge, and with its unique oxide transformed the transistor into the integrated circuit. Optoelectronics, however, which complements Si electronics, would not have been possible without the III–V semiconductors, and their direct-gap capability making possible efficient light emission (see the discussion in [1]) and, as we shall see, heterojunctions and much more.

In my view, optoelectronics really began when Rediker's Lincoln Laboratory group reported (at the 1962 IRE Solid State Device Research Conference) using a simple Zn-diffused GaAs p-n junction [2] to generate infrared radiation and transmit signals over appreciable distances [3]. If recombination radiation could be used to broadcast a signal over such a long distance, it made sense to try to make the direct-gap III–V p-n junction into a laser, which was accomplished in 1962 with GaAs and with the prototype visible-spectrum alloy $GaAs_{1-x}P_x$ (see [1] and [4]–[11]). The semiconductor laser raised optoelectronics to a new level. It also presented many new problems, and opportunities, many difficult to anticipate, including the main topic of this paper—impurity-induced layer disordering (IILD) [12]–[16]. We discuss here how IILD occurred, and its basic significance.

II. Thin-Layer Heterojunction

From the beginning in 1962 and the demonstration of the semiconductor laser, and with it the problem of adequate carrier and photon confinement in a Zn-diffused III–V homojunction, which approximates a "weak" form of p-i-n, [1] it was clear that the double heterojunction (DH) [17], [18], a "strong" form of p-i-n (i.e., one providing good photon as well as carrier confinement), was required for semiconductor lasers. Although epitaxial III–V heterojunctions were grown as early as 1960 (when, in fact, the epitaxial growth and the device use of III–V alloys were initially demonstrated) [19], [20], lattice-matched heterojunctions (DH's) were first realized later with the development of the AlGaAs–GaAs system in 1967 [21]. Then, with the double heterojunction, it was only a question

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of time till the old idea of quantum size effects (QSE's, "the particle in a box") would be manifest with shrinking of layer dimensions, or with replication of thin DH layers into superlattices (SL's) [22]. Note that QSE's in a semiconductor were known in J. Bardeen's laboratory (Urbana, IL) in the early and mid-1950's when Bardeen had Schrieffer work on the conductivity of a thin Ge inversion layer, a carrier-confining layer of quantum-well (QW) thickness ("size"). Clearly then it would be possible to observe QSE's with III–V heterostructures as they reached QW dimensions ($\leq$500 Å), which is more a question of technology than basic principle.

At first, it was thought that only a crystal growth technology such as molecular beam epitaxy (MBE) could grow QW's and superlattices (SL's), which, indeed, was a myth that was easily disproved by the demonstration of liquid phase epitaxial (LPE) InGaAsP–InP p-n QW lasers [23], [24]. These were, in fact, the first QW diode lasers (1977), followed then by $Al_xGa_{1-x}As$–GaAs p-n QW lasers grown (1978) by metal–organic chemical vapor deposition (MOCVD). Although not the first p-n QW laser [1], $Al_xGa_{1-x}As$–GaAs QWH's grown by MOCVD [25] had the distinction of being the first to operate continuously (CW) at 300-K [26]–[29], thus establishing further the practicality of the QW in semiconductor lasers. Starting as a Zn-diffused p-n homojunction and then becoming a double heterojunction, the semiconductor laser in now its new metamorphosis would bit by bit become universally a QW device. Also $Al_xGa_{1-x}As$–GaAs would persist in acting as the prototypical QW and superlattice heterostructure system. The $Al_xGa_{1-x}As$–GaAs system proved to be valuable in revealing much more, including the impurity-induced layer disordering (IILD) of interest here.

III. Thin-Layer Heterostructure Technology

Contrary to some opinion that the first p-n QW lasers were realized by MBE or MOCVD crystal growth, the first QW diode lasers, as already mentioned, were grown in 1977 in Urbana by LPE [23], [24], [30] (see [1, Fig. 7]), and were first reported at the 1977 IEEE Device Research Conference (DRC, Cornell University, Ithaca, NY). At the same conference Dupuis reported the successful use of MOCVD, a form of vapor phase epitaxy (VPE), to grow conventional double heterojunction $Al_xGa_{1-x}As$–GaAs lasers that operated CW at room temperature [31], [32]. The III–V constituent Al at last could be used successfully in the VPE growth of heterojunctions. This was an important development because previously LPE was the method of choice to grow CW 300-K $Al_xGa_{1-x}As$–GaAs double heterojunction lasers. I had already considered (1975–1977) VPE as a preferred way to grow QW heterostructures (QWH's) and SL's [1], and consequently at DRC asked Dupuis and Dapkus to start growing for us—in a much better controlled MOCVD process than our LPE process—$Al_xGa_{1-x}As$–GaAs QWH's with more refined geometries and a wider choice of QW parameters than we could conveniently reach with LPE. It merely remained to see whether Dupuis' MOCVD $Al_xGa_{1-x}As$–GaAs QWH's were of good quality. Barrier layer and well size (thinness) was not an issue because Dupuis had made and was operating a cleverly constructed, electronically valved MOCVD reactor [25]. He could reach and reproduce any thin layer dimension ($<$10 Å) that we wanted. By late 1977 and early 1978, he could supply us with $Al_xGa_{1-x}As$–GaAs QWH crystals as fast as we could evaluate them and propose new ideas.

Over the years, we had become quite proficient in photopumping thin semiconductor laser samples, which was a convenient way to evaluate and study various III–V materials and heterostructures. We were experienced not only in growing III–V semiconductors (e.g., visible-spectrum III–V alloys), but also in preparing thin samples ($\sim$1 μm), cleaving and handling small samples, and heat sinking them in a special way (compressed) in metal under sapphire or diamond for photopumping [33]. For example, by these methods not only did we establish that $In_{1-x}Ga_xP$ was capable of laser operation [34]–[37], but also that its surface recombination velocity was much smaller than that of GaAs [35], [38], [39]. By the time of the 1977 DRC, we were well prepared to study LPE or MOCVD QWH's. For our first experiment in photopumping an $Al_xGa_{1-x}As$–GaAs QWH, I asked Dupuis to grow a simple single-well QWH with a 1 μm lower $Al_{0.6}Ga_{0.4}As$ confining layer adjacent to the GaAs substrate, then a 200-Å GaAs QW, and finally a 0.1 μm $Al_{0.6}Ga_{0.4}As$ confining layer on top. The substrate was selectively removed, which became a routine procedure in all further experiments, so that only QW GaAs stimulated emission would be observed, and not substrate "light," and not indirect-gap ($x \sim 0.6$) confining-layer "light." We note that without the substrate, the single-QW crystal appeared red because we could see through 200 Å of GaAs, and $1 + 0.1 = 1.1$ μm of $x \sim 0.6$ $Al_xGa_{1-x}As$ appeared red. The appearance of substrate-free MOCVD $Al_xGa_{1-x}As$–GaAs QWH's or SL's turned-out to be important in our later work, including in the discovery of IILD. We expected to see red QWH platelets, the usual observation, and not some other color.

The 200-Å GaAs QW of our first MOCVD QWH was big enough to be an effective collector of photogenerated electron-hole pairs [40], and led immediately to photopumped laser operation at 77 K in an unusually wide spectral range ($\Delta\hbar\omega \sim 300$ meV, [1, Fig. 10]) and to also the first CW 300-K laser operation of a QWH [26] (cf. [1, Fig. 11]). Multiple-well MOCVD $Al_xGa_{1-x}As$–GaAs QWH's proved to be equally interesting. For example, small rectangular single- and multiple-QW samples free of substrate crystal exhibited phonon-assisted laser operation [41]–[43], which alerted us to the fact that phonon effects could be of some importance. These various experiments along with a few further experiments in conventional thermal annealing [44] of MOCVD $Al_xGa_{1-x}As$–GaAs QWH's in order to shift QW energies to higher values [45], [46], which requires relatively high temperatures ($\gtrsim$900 °C) and long annealing periods ($\gtrsim$10 h), provided us with enough background and experience for what was about to occur—the discovery of impurity-induced layer disordering (IILD), or simply layer disordering (LD).

IV. Superlattice Disordering

It is questionable how important superlattices (SL's) are in practical devices, but they play a useful function in the study of QW phenomena. For example, it is difficult to make an absorption measurement on a single GaAs QW, but QW's replicated into a SL provide enough GaAs to make absorption measurements convenient. These reveal at 300 K the QW confined-exciton states, which act furthermore as markers showing how the entire Γ band (not just a band edge) shifts with pressure [47], [48].

The SL made it convenient to consider other problems, e.g., the problem of heterointerface perfection and whether CW 300-K laser operation of a SL might even be possible. Since we were able to demonstrate this possibility [49], and knew, in contrast, that an equivalent thickness ($\sim$1 μm) of bulk GaAs does not operate as a photopumped CW 300-K laser because of its high surface recombination velocity [38], [39], we established, based on these data [49], that the mini-band transport of a high quality (laser-quality) $Al_xGa_{1-x}As$–GaAs SL was weak. In other words, electron-hole pairs do not recombine nonradiatively at the heterointerfaces within an MOCVD $Al_xGa_{1-x}As$–GaAs SL, nor do they transport to and recombine at the sample surface.

As we attempted to reduce QW sizes further and further to realize shorter and shorter wavelength laser operation, smaller size no longer had an effect, which is an expected effect of III–V alloy clustering [50]. The question of alloy clustering, and its scale, occurred off and on from the time of the first construction of $GaAs_{1-x}P_x$ junctions in 1960 [19], [20], and then with the use of this prototype III–V alloy in lasers and LED's in 1962 [6]. In spite of any clustering, the $GaAs_{1-x}P_x$ alloy was "smooth" enough to support stimulated emission. To check the possibility of clustering in $Al_xGa_{1-x}As$–GaAs QWH's and SL's we resorted, after some argument, to employing AlAs (binary) coupling barriers. The all-binary SL's behaved as expected and operated as CW 300-K photopumped lasers, another success of MOCVD crystal growth [25], but what was there to report concerning stimulated emission in an all-binary SL since we already knew that $Al_xGa_{1-x}As$–GaAs SL's were capable of CW 300-K laser operation?

Since I knew that phonon effects were observable in QWH's [41]–[43], I was of the opinion that our undoped SL's should be turned into doped SL's by Zn diffusion. Maybe then phonon replicas involving the Zn impurity would be observable. I asked W. Laidig (graduate student) to diffuse Zn into the AlAs–GaAs SL ($L_B \sim 150$ Å, $L_z \sim 45$ Å) to a concentration in the range 10^{17}–10^{18}/cm^3. I knew from much earlier work that a Zn concentration of 10^{17}–10^{18}/cm^3 in GaAs was observable in photopumping as a conduction band to acceptor laser transition (acceptor not smeared into the valence band) [51]. Maybe the Zn acceptor could be put to use in photoluminescence (PL) studies on our all-binary SL's.

Laidig objected to my request to perform a $\sim$1-μm deep diffusion of so low of an impurity concentration, $n_{\mathrm{Zn}} = 10^{17}$–$10^{18}$/cm^3. This would take too long for the Zn diffusion to penetrate $\sim$1 μm at so low of a doping level, so I agreed, "Fine, raise the temperature enough to do a convenient Zn diffusion to a depth of $\sim$1 μm." We compromised and used a $ZnAs_2$ source to diffuse Zn (in a closed ampoule, Nov. 1980) into the AlAs–GaAs SL ($L_{\mathrm{B}} \sim 150$ Å, $L_z \sim 45$ Å) at 575°C for 4 h. We were surprised at the result, which would have been missed if we did not routinely remove the GaAs substrate from our QWH and SL samples. The thin samples were single crystalline and with the substrate removed appeared thin, shiny, transparent, and pale yellow, and not at all like the thin red as-grown SL we had already operated as a CW 300-K photopumped laser [52]. The average composition of the crystal was preserved; it merely transformed from SL layered form (a coarser "alloy") to the same average composition bulk crystal (a finer scale alloy). The crystal transformed from "red" gap SL to "yellow" gap bulk crystal, a fundamental and an important practical effect. We wanted to be sure of what we had done, which we knew at once was the intermixing and conversion of the AlAs–GaAs SL to bulk-crystal $Al_xGa_{1-x}As$ ($x \sim 0.77$). To be certain of the Zn impurity's role, we repeated the 575 °C, 4-h annealing schedule with only excess As in a sealed ampoule with another sample of the as-grown SL. The crystal remained "red" SL, and operated as a CW 300-K laser unchanged from the as-grown crystal [52].

To show others what we had discovered, i.e., impurity-induced layer disordering (IILD) [52], we repeated the Zn diffusion ($ZnAs_2$, 575 °C, 10 min) on another sample of the same AlAs–GaAs SL prepared with Si_3N_4 masking stripes on the surface to show by direct comparison the effect of impurity diffusion (bare surface) and simple annealing (masked surface). We demonstrated IILD via the slant cross section of Fig. 1 [52], [53]. The stripe region with the SL layers smeared shows the effect of the Zn diffusion. Impurity diffusion in minutes (<10 min) disordered most of an AlAs–GaAs SL that ordinary annealing at the same temperature (575 °C) did not change appreciably in hours (4 h) [52].

It was known immediately that IILD was a basic effect with practical implications, as well as the basis for a patent application [54], [55]. For example, we could use IILD to form simply and very generally lower gap QW or SL regions, of any shape or form, surrounded with higher gap disordered (or intermixed) bulk crystal. Lower gap QW active regions (red) could be imbedded in higher gap bulk crystal (yellow) of lower index of refraction and, thus, with the capacity to confine carriers and photons. This clearly had use in laser devices and in optoelectronics more generally. We showed this first on the same SL as that of Fig. 1 by forming the square array SL dot pattern (red) of Fig. 2 imbedded in higher gap $Al_xGa_{1-x}As$ ($x \sim 0.77$, yellow) [56]. Cleaved samples of red AlAs–GaAs SL, the square array dot pattern of Fig. 2, imbedded in higher gap (yellow) bulk-crystal $Al_xGa_{1-x}As$ ($x \sim 0.77$) easily operated as CW 300-K photopumped lasers [56]. The SL dots served as the active material, and the overall cavity was defined by the higher gap IILD alloy. It was known that many device configurations could easily be rendered by IILD, and this proved to be correct as discussed elsewhere [57].

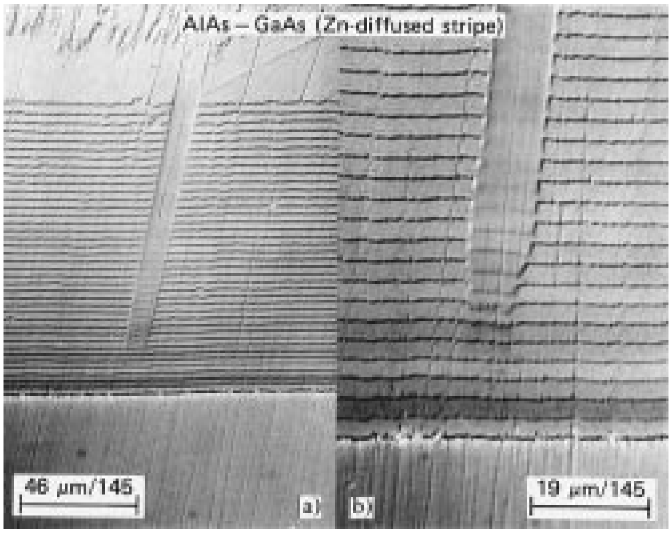


Fig. 1. Shallow-angle ($\sim$0.4°) slant cross section of an AlAs–GaAs superlattice (SL) sample that, except for a $\sim$10 μm stripe opening, has been masked with Si_3N_4 and been Zn diffused ($ZnAs_2$, 575 °C, 10 min). The shallow-angle magnification is $\sim$145× in the vertical direction (no horizontal magnification) and is skewed somewhat relative to the orientation of the Zn-diffused stripe. In the region of the Zn diffusion, the 40-period AlAs–GaAs ($L_B \sim 150$ Å, $L_z \sim$ 45 Å) SL has become compositionally disordered indirect-gap $Al_xGa_{1-x}As$, ($x \sim 0.77$), changing color from red to yellow (7680–5900 Å) (after [52]).

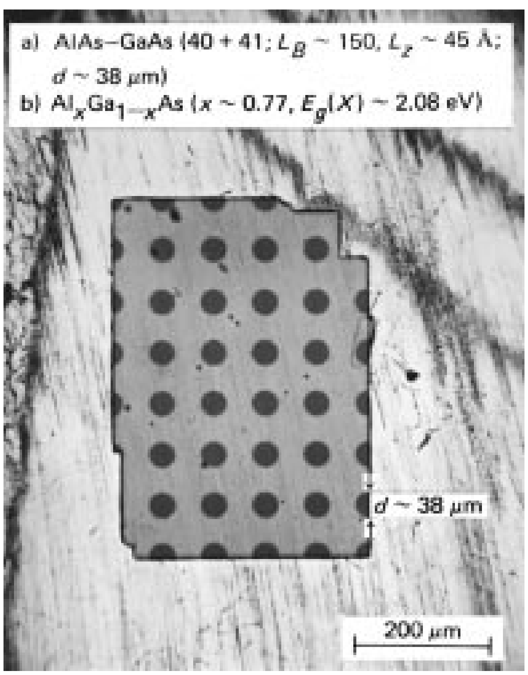


Fig. 2. Square array of (a) AlAs–GaAs ($L_B \sim 150$ Å, $L_z \sim 45$ Å) superlattice dots (“red” 38-μm disks) surrounded by (b) yellow-gap $Al_xGa_{1-x}As$ ($x \sim 0.77$, $E_g \sim 2.08$ eV) formed by impurity-induced layer disordering (intermixing, IILD) accomplished by Zn diffusion ($ZnAs_2$, 575 °C, 30 min). The cleaved sample of yellow IILD $Al_xGa_{1-x}As$ with red AlAs–GaAs SL disks (dots) is compressed in In (after [56], in color).

V. QW Layer Disordering (Intermixing)

As is well known, $Al_xGa_{1-x}As$–GaAs QWH’s or SL’s are quite stable against ordinary thermal annealing [44]. In fact, high temperatures and long annealing periods are required to effect much of a change in QW energies [45], [46], and ordinary annealing is not even considered for total intermixing of QW’s and heterobarriers. This is consistent with a related example: many years ago I knew (see [19], [20]) that the proposal to make $GaAs_{1-x}P_x$ by diffusing P into GaAs [58], which some researchers “re-invented” (unsuccessfully) in 1962 wishing to make III–V alloy lasers, did not make sense because the crystal atoms simply could not be moved, from a surface source (P), and be put into place fast enough deeper in the crystal (GaAs) by this form of “self-diffusion.” In other words, to form the III–V alloy the constituent atoms of the crystal have to be moved more quickly and efficiently, for example, by a process such as VPE or LPE. Ordinary diffusion did not make sense for III–V alloy formation, nor for QW-barrier intermixing, which made IILD come as a surprise.

Because I knew of J. Bardeen’s long interest in diffusion, I wanted him to see our IILD results, the transformation of a “red” AlAs–GaAs SL into “yellow” $Al_xGa_{1-x}As$ alloy. Normally, Bardeen visited the laboratory about every two or three weeks for discussions on various matters, including semiconductor research. When we showed him IILD late in 1980 (after he returned from a trip), he immediately understood the significance of the red–yellow transformation from SL to bulk-crystal alloy. Unlike his usual pattern of visiting, he then returned three days in a row for extended discussions to help propose an explanation. His interest in diffusion, self-diffusion, and crystal rearrangement was as strong in 1980 as in 1952–1954, and even earlier. I knew from long contact with Bardeen that his memory and effectiveness on problems of earlier interest to him did not fade with time [59]. His memory was very good, and he did not have to relearn an older area of interest to use the ideas in a new context, now IILD. I was sure IILD would interest him, and it did. All that Bardeen needed in order to help in explaining IILD was to first read several of our references on Zn diffusion in GaAs, and to become familiar with the interstitial-substitutional behavior of Zn [60]. Fig. 3 shows his handwritten contribution to the first publication we prepared on the subject [52]. In a few places on Fig. 3 are pencil clarifications (N.H.) for ease in typing. Fig. 4 shows the cover letter I wrote to the editor [52] concerning our manuscript, which we knew had basic significance. The figure does not show my later hand written note requesting that our manuscript not be sent to certain individuals having a hard time understanding that LPE and MOCVD grew QWH’s and SL’s just as surely as other methods, and that we were not observing weaknesses related to methods of crystal growth.

The two-site behavior of the Zn acceptor in III–Vs (GaAs) was, of course, the key issue in causing IILD. Because of the opposite gradient in Al and Ga concentration at an $Al_xGa_{1-x}As$–GaAs heteroboundary, the Al on one side can compete with the Ga on the other side for a Column III site, let us say, a vacancy (V). Either can fill the vacancy, which insures IILD. The only real issue is that of the presence of vacancies, which is inherently part of the interstitial-substitutional diffusion of Zn in the GaAs family of III–Vs. The substitutional Zn, Zn_s, or interstitial Zn, Zn_i, is not necessarily isolated in the crystal lattice [52]. A substitutional Zn atom, Zn_s, can move into an interstitial site forming a

1 $Zn_i + V^0$

The fact that diffusion of Zn greatly enhances[2] the interdiffusion of Ga and Al in the superlattice heterostructures[3] indicates that a modification of the interstitial-substitutional mechanism for Zn diffusion ~~requires modification~~ is required. It is suggested that a closely associated Zn-vacancy pair formed by substitutional Zn moving into a neighboring interstitial site forms an intermediate link between purely interstitial and substitutional Zn according to the reaction[4]

$$Zn_i^+ + V^\circ \rightleftarrows [Zn_i, V]^+ \rightleftarrows Zn_{Ga}^- + 2h^+. \qquad (1)$$

Here V° indicates a neutral vacancy and h a hole. Neighboring Ga and Al atoms could move into the vacancy of the $[Zn_i, V]$ pair but the Zn_i would remain attached. In this way, interdiffusion of Ga and Al would be promoted as well as providing an additional mechanism for Zn diffusion.

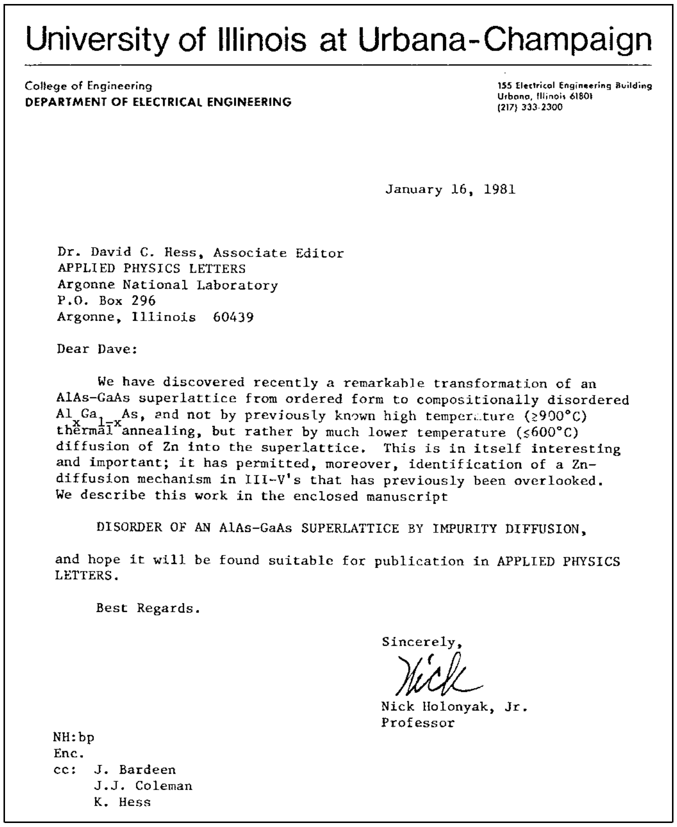
¶ The total Zn concentration is $c = c_i + c_p + c_s$, where c_i is that of isolated Zn interstitials, c_p that of $[Zn_i, V]$ pairs and c_s that of substitutional Zn. It is assumed that $c_i \ll c_p \ll c_s$, so that $c_s \cong c$. According to the laws of mass action,

$$c_p = K_1(T)\, c_s\, p^2 = K_2(T)\, c_i\, c_v, \qquad (2)$$

where c_v is the concentration of isolated neutral vacancies. If the motion of pairs dominates the Zn diffusion, the diffusion rate should be proportional to the square root of the As_2 vapor pressure, p_{As_2}. Data on Zn diffusion in $Ga_xAl_{1-x}As$ $Al_xGa_{1-x}As$ at higher temperatures indicates that D_{eff} varies inversely with $p_{As_2}^{1/2}$ which shows that interstitial diffusion of Zn dominates over pair diffusion.

K_1 C_v p_{As_2} D_{eff}

Fig. 3. J. Bardeen's hand-written contribution to [52], the first paper on impurity-induced layer disordering (Zn IILD) of an AlAs–GaAs superlattice (SL). Clarifications written by N.H. for ease in typing are evident.



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January 16, 1981

Dr. David C. Hess, Associate Editor
APPLIED PHYSICS LETTERS
Argonne National Laboratory
P.O. Box 296
Argonne, Illinois 60439

Dear Dave:

We have discovered recently a remarkable transformation of an AlAs-GaAs superlattice from ordered form to compositionally disordered $Al_xGa_{1-x}As$, and not by previously known high temperature (≳900°C) thermal annealing, but rather by much lower temperature (≲600°C) diffusion of Zn into the superlattice. This is in itself interesting and important; it has permitted, moreover, identification of a Zn-diffusion mechanism in III-V's that has previously been overlooked. We describe this work in the enclosed manuscript

DISORDER OF AN AlAs-GaAs SUPERLATTICE BY IMPURITY DIFFUSION,

and hope it will be found suitable for publication in APPLIED PHYSICS LETTERS.

Best Regards.

Sincerely,

Nick

Nick Holonyak, Jr.
Professor

NH:bp
Enc.
cc: J. Bardeen
J.J. Coleman
K. Hess

Fig. 4. Cover letter accompanying the manuscript of [52], indicating the basic significance of IILD.

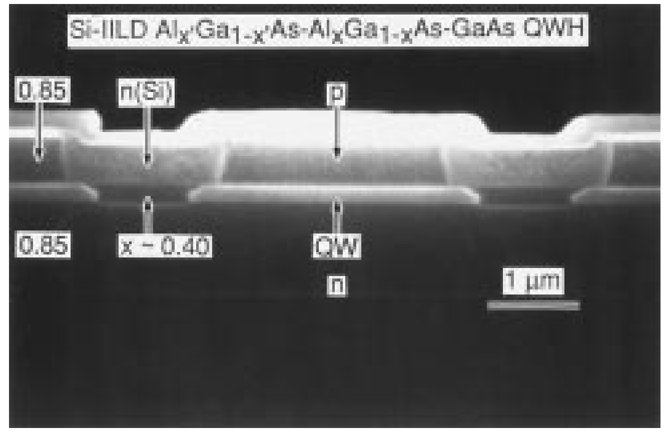

Fig. 5. Scanning electron microscope image of the cross section of a ten-stripe Si-IILD $Al_xGa_{1-x}As$–GaAs coupled stripe laser array. The QWH laser stripes are 3-μm wide with 1-μm n-type Si disordered regions between the p-type stripes. The Si diffusion performed at 816 °C (10 h) (after [72]).

Zn_i–V pair, which does not necessarily dissociate. The pair vacancy is available, nevertheless, for Al or Ga occupancy (IILD), which merely means the Zn_i–V pair can move and repeat its behavior. This contributes further to IILD and to Zn diffusion itself. Not only does the Zn_i–V pair support IILD, it serves also as a diffusion mechanism in its own right. Paired with a Zn interstitial, Zn_i, the vacancy V becomes more mobile. This is seen by noting how immune, how resistant to change an AlAs–GaAs SL is to ordinary thermal annealing (∼900 °C, ∼10 h) and how easily it disorders with Zn diffusion at much lower temperature (∼600 °C, ∼10 min).

VI. Generality of Layer Disordering

Once the two-site behavior of Zn in disordering a III–V QWH or SL was established, I knew at once of other two-site impurity species with which to attempt IILD [61]–[63]. This was a consequence of working with the amphoteric dopants Ge and Si in GaAs as early as 1961 (at General Electric, Syracuse) for the purpose at first of making an all-Ge doped tunnel junction (p_{Ge}–n_{Ge}), and later Si-doped junctions (p_{Si}–n_{Si}) for more efficient light emitters and lasers. Temporarily bypassing the possibility of IILD by diffusion of Si, which has a much lower vapor pressure and is more complicated to diffuse than Zn, I wanted to implant Si in an AlAs–GaAs SL, but B. Streetman, our expert in implantation (Urbana, IL), was not equipped with the Si dopant on his implanter. When I mentioned this to G. Stillman, he proposed that M. Feng (Hughes), for whom he consulted, would implant some samples that Stillman could hand-carry to be implanted. After annealing these Si-implanted SL samples, as well as some samples implanted with other species, we immediately achieved IILD [61], [62]. After some differences in opinion on acquiring more partners, this work was repeated and then reported [64], [65]. Later we realized that in some cases we had annealed the implanted SL samples at too low of a temperature and that implant species other than just Si, at higher annealing temperatures, could be used successfully in layer disordering [66]. Some implant species, the two-site diffusants, were active in disordering, and others merely introduced damage (and vacancies) that nevertheless promoted disordering. Also it was clear that mismatch and strain could play a role [67], and that IILD could be realized quite generally by various methods in a variety of III–V QWH's and SL's.

In the case of the Si impurity itself, a more important development was to employ it, a donor, in diffusion to effect IILD [63], [68]. Diffusion, for us, was a much more convenient and less costly process than implantation. Because n-type GaAs substrates are more prevalent and QWH's are grown most conveniently and practically with thin p-type layers on top, a donor, Si, is vital in IILD to provide higher gap n-type crystal to define and confine p-type active regions. Both carriers and photons are confined by the n-type IILD bulk crystal, which obviously has a purpose in laser devices (e.g., see [16]) and in optoelectronics more generally.

Because of the nature of the Si diffusion "recipe" we used for IILD of $Al_xGa_{1-x}As$–GaAs QWH's and SL's [68], i.e., the use of a thin layer of Si (∼100 Å) capped with a thicker layer of SiO_2 (≳2000 Å) deposited on the crystal surface, it was inevitable that we would try impurity-free layer disordering. I was a witness (1955) to Frosch's discovery of the oxide masking of Si [69], [70] and had many years of experience with Ga diffusion in Si through an oxide layer. I knew that Ga, because of the Si diffusion "recipes" we employed, could out-diffuse through the oxide cap used in our Si IILD experiments, thus acting as a vacancy source. All we really had to do was to try the experiment, which, indeed, worked [71]. We showed

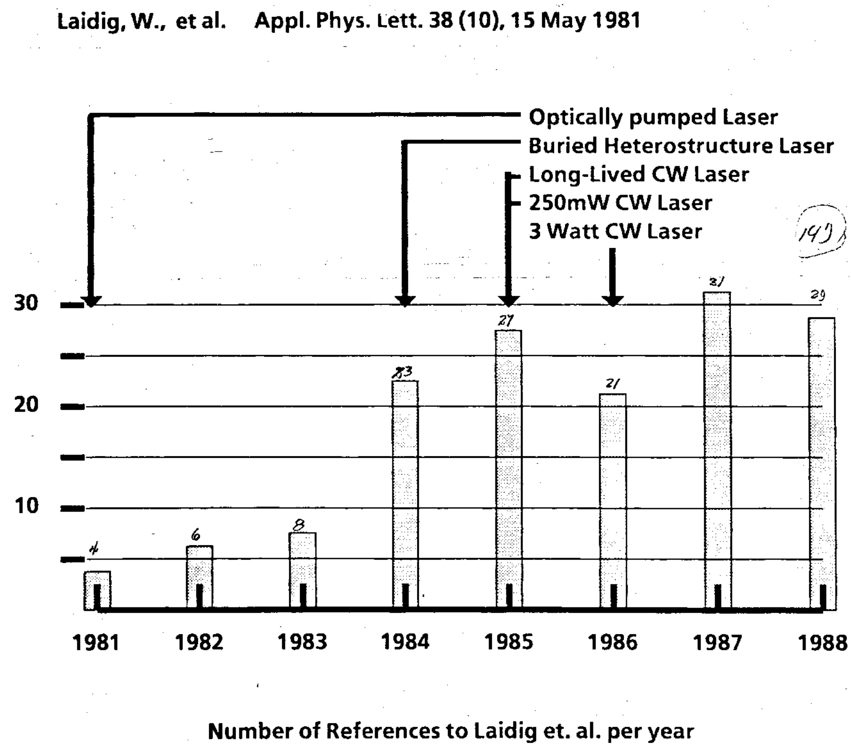

Fig. 6. The number of articles per year published from 1981 to 1988 making reference to the IILD paper of [12] and showing the pattern in growth of IILD research. (Courtesy of R. Thornton, Xerox, Palo Alto, CA.)

it was possible to disorder a QWH SL by an impurity-free vacancy process [71], which was revealing in showing further how general QWH layer disordering could be.

VII. Implications of QW Layer Disordering

We knew from the beginning of IILD that it offered many device applications, which was, of course, the reason to seek patent coverage. Impurity induced layer disordering is an ideal planar method, a maskable method, to form passive or active waveguide regions in QWH's. An example, a relatively sophisticated device, is the coupled ten-stripe QWH $Al_xGa_{1-x}As$–GaAs laser of Fig. 5 [72]. At the center of the figure (end view at a facet cleave) is the as-grown QWH with $\sim$1 μm wide Si-IILD higher gap n-type bulk crystal on either side of the lower gap QWH stripe active region(s). A more recent example employing Zn IILD is the multiple stripe laser of [73] which, using antiguiding, is complementary to the multiple stripe (guiding) laser of Fig. 5. Other examples realized sometime ago are cited in [16].

Overall there may now be as many examples of applications of IILD in lasers, waveguide structures, integrated optoelectronic components, etc., as there are groups interested in IILD, practicing IILD, and studying IILD, which is large but which, of course, was not the case in the beginning. When we first reported IILD, some research groups were at first skeptical, and considered our results an anomaly, a weakness of our QWH and SL crystals (an unwarranted assumption). For several years, as shown in the citation count of Fig. 6, not many workers paid much attention to IILD. But then around 1984 (Fig. 6), the number of publications dealing with IILD began to grow. Now there are many contributions to IILD and many extensions from the $Al_xGa_{1-x}As$–GaAs system to other III–V systems, some as simple as the recently reported case of the use of IILD to make higher gap (less absorptive) protective windows in the mirror region of $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ QWH lasers in order to realize higher power operation [74]. Who knows how many IILD applications, in how many different III–V systems, are possible or will occur? The answer is as many as we now see and as many as an expanding field of IILD researchers can devise as the III–V art keeps developing. It will all depend on how big LED, laser, and optoelectronics science and technology become, which indeed show no sign of slowing down or stopping.

If there were no device and optoelectronics applications for IILD (in fact, there are many!), it would still have importance. In some respects, the term "disordering," or IILD, is a misnomer. In some average sense a QWH or SL, say in the AlAs–GaAs system, is "lumpy." Layering, even on a fine scale, gives a "lumpy" structure. Impurity induced layer disordering (IILD) operates to smooth the system (the layered "alloy"), which on the average is then smoother albeit stochastic in the Al–Ga arrangement. Nevertheless, IILD smooths a crystal, and, in retrospect, we can see the effect of this in much earlier work.

My first student was C. M. Wolfe. When he described his work and studies on $GaAs_{1-x}P_x$ (GaAs–GaP) to his doctoral committee, he was asked by a physics department faculty member, "What about ordering, As–P ordering?" Neither Wolfe nor I was impressed much by the question, considering what the problems were (in 1963–1965) in simply growing $GaAs_{1-x}P_x$ [19], [20], [75], [76]. Just how were we expected

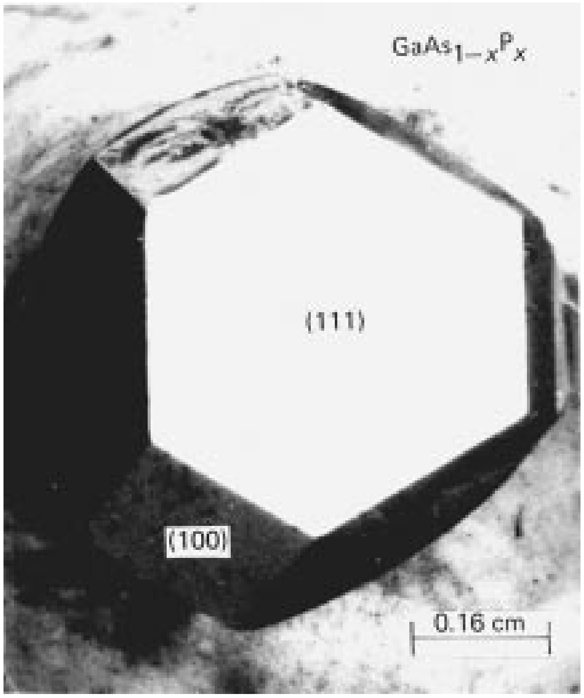

Fig. 7. Zn-doped $GaAs_{1-x}P_x$ crystal grown by vapor phase epitaxy showing the tendency toward single-crystal formation and the development of $\{111\}$ and $\{100\}$ natural facets. Zn IILD operates to smooth the crystal growth.

to see ordering, particularly in $GaAs_{1-x}P_x$ that was doped to make lasers (p-n junctions)?

We illustrate (explain) this, the effect of impurity "smoothing," by considering the $GaAs_{1-x}P_x$ crystal of Fig. 7. The manner in which low-index III–V crystal facets developed during the growth of the crystal (only some crystals) is shown in the figure, which shows 562 mg of $GaAs_{1-x}P_x$ grown via co-transport of GaAs and GaP with iodine or chlorine in a closed-tube ampoule (temperature 750 °C–850 °C) [19], [20], [75], [76]. The $GaAs_{1-x}P_x$ seeded spontaneously at the small constricted end of the ampoule, which was ~10 °C cooler than the source GaAs and GaP. As the crystal grew slowly over a period of about a week, one of the spontaneously seeded crystallites predominated, and only the dense $\{111\}$ and $\{100\}$ facets evident in Fig. 7 developed. The slow growth normal to these dense planes and the random walking of the atomic constituents along the planes insured extremely smooth natural crystal facets (Fig. 7).

There is now a further matter: the crystal of Fig. 7 was grown with Zn doping, which, as a "recipe," yielded single crystal (Fig. 7) much more readily than donor doping. Why should this be; is it the effect of a two-site impurity? The point is that Zn IILD was at work, although in a more complicated manner than in the case of the AlAs–GaAs system (simple Column III disordering, Al–Ga intermixing, randomization, "smoothing"). The IILD operated very effectively on the GaAs–GaP system [67] (Column V disordering) and a situation of more mismatch and strain [67], and with perhaps the participation also of antisite defects. In other words, as the Zn was at work helping to shuffle and move Ga atoms around, As and P rearrangement also occurred, thus relieving strain and smoothing the crystal and helping to promote (p-type) single crystal growth.

After we knew about IILD in the Fall of 1980, we could more readily account for the form of the $GaAs_{1-x}P_x$, p-type single crystals versus n-type poly-crystals, grown by vapor phase epitaxy much earlier [19], [20], [75], [76]. Also we could begin to understand why we would not have been able to observe III–V alloy ordering in 1962–1965, not in the case of doped crystals and with doping impurities promoting IILD and crystal smoothing. Furthermore, in a system such as InP–GaP, one of greater mismatch (and potentially more strain), and a greater tendency to order, it was apparent that Zn IILD would be very effective in promoting disordering [77], [78]. After we knew about IILD, we knew also that IILD (dopants) played a role in smoothing III–V alloys and in smearing, moreover, heterointerfaces. In fact, maybe IILD should have been observed before we diffused Zn into an AlAs–GaAs SL and observed such a striking metamorphosis, the change from red-gap QW crystal to yellow-gap bulk crystal.

VIII. Conclusion

In view of the great stability of a GaAs or SL, say AlAs–GaAs ($Al_xGa_{1-x}As$), against ordinary thermal annealing, impurity-induced layer disordering (IILD, or layer intermixing) came as a considerable surprise, specifically, the lower temperature (selective) change of a QW red-gap crystal to a yellow-gap bulk crystal. Besides being a fundamental effect, the IILD change of a QWH or SL from QW lower bandgap to bulk-crystal higher gap has proven to be a powerful method (a planar technology) to confine carriers and photons. Layer disordering (IILD) obviously has many uses in laser, waveguide, and optoelectronic devices. The number of applications continues to grow, with also a growing list of III–V systems (AlAs–GaAs, GaAs–GaP, AlAs–GaAs–InAs, InP–GaP–AlP) amenable to IILD. Particularly notable are the III–V systems employing Al and Ga, which easily substitute for one another.

In the usual "mechanics" of atomic diffusion in a crystal, the motion of a lattice constituent is not apparent. A process that is microscopic and hard to see becomes macroscopic and visible in the case of IILD of a QWH or SL. Lower temperature controllable, i.e., selectable (maskable), layer intermixing (IILD) displays on a larger scale the lattice-atom rearrangement that occurs on a microscopic scale. In other words, IILD and its low-gap/high-gap transformation of a QWH or SL is useful not only for carrier and photon confinement, and thus device applications; it is useful also as a powerful method to study diffusion. Now that we know about IILD, and have a method to see small scale changes (atomic rearrangement) amplified in essence into large scale layer changes, not to mention in a controllable form or geometry, we have a powerful way to study diffusion itself. This may be one of IILD's more important uses.

As this special journal issue indicates—by the number of research groups, articles, references, subjects—impurity induced layer disordering (IILD) is broadly based and growing. This includes now (since 1980) more III–V QWH and SL systems, more different devices and applications, and more methods to perform layer disordering. It is safe to assume IILD, a unique planar optoelectronics technology, will continue to thrive, in fact, expand because of its (QW lower gap, bulk-crystal higher gap) capability to confine carriers and photons. On the practical side, besides the increasing scope of its use in QWH optoelectronic applications, it will be interesting to see how fine the rendering of IILD dimensions becomes. In terms of fundamental studies, it will be interesting to see how IILD will be used to study diffusion in III–V systems, and whether IILD can be used to study diffusion in other layered systems.

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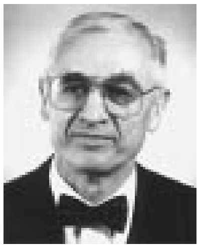

Nick Holonyak, Jr. (S'51–A'55–M'59–SM'62–F'67–LF'94) was born in Zeigler, IL, on November 3, 1928. He received the B.S. (1950), M.S. (1951), and Ph.D. (1954) degrees in electrical engineering from the University of Illinois.

A Texas Instruments Fellow, he was John Bardeen's first student. He later was employed as a Member of Technical Staff at Bell Telephone Laboratories (1954–1955) and helped demonstrate feasibility of diffused-impurity silicon devices, including transistors, oxide-masked 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) where he made contributions in the areas of power and signal p-n-p-n devices (including invention of the shorted-emitter and symmetrical SCR and thyristor switches—TRIAC's, etc.), tunnel diodes, phononassisted tunneling (the initial observation of inelastic tunneling and the beginning of tunneling spectroscopy), halide transport, and epitaxial growth of III–V compounds and compound mixtures (1960–1963), double injection and deep-impurity-level effects, junction luminescence (GaAsP LED's), and III–V alloy semiconductor lasers (visible spectrum, GaAsP, 1962). His work from 1960 to 1962 on GaAsP and the initial construction in 1960 of a p-n junction in this crystal system, and a visible-spectrum laser in 1962, led to the commercial introduction of GaAsP LED's. He is the inventor of the first practical light-emitting diode (the GaAsP LED), which also marks the beginning in the use of III–V alloys in semiconductor devices. Since 1963, he has been a Professor at the University of Illinois in the Department of Electrical and Computer Engineering and is a member of the University of Illinois Center for Advanced Study. He and his students have worked primarily on III–V semiconductors, III–V alloy crystal growth, and the 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 $In_{1-x}Ga_xP_{1-z}As_z$. He and his students were the first to make quaternary III–V semiconductor devices (LED's and lasers). His research since 1976 has been concerned with quantum-well light emitters and lasers, and with impurity-induced layer disordering, which shifts lower gap quantum well layers to higher gap bulk crystal and serves as a basis for integrated optoelectronic devices. In 1990, he and his students introduced higher temperature ($\geq$400 °C) stable native oxides on Al-bearing III–V compounds and demonstrated their use in optoelectronic devices (LED's and lasers). He and his students were the first (1977) to construct p-n quantum-well lasers (InP–InGaAsP, LPE) and then were the first to achieve (1978) continuous (CW) room temperature (300 K) laser operation of quantum-well heterostructures and superlattices, and later (1982) strained layer quantum-well heterostructures. They are the source of the name "quantum-well laser." He is co-author of the book *Semiconductor Controlled Rectifiers*, (Prentice-Hall, 1964) and *Physical Properties of Semiconductors* (Prentice-Hall, 1989), editor of the Prentice-Hall series "Solid State Physical Electronics," and has served on the Editorial Board of the PROCEEDINGS OF THE IEEE (1966–1974), *Solid-State Electronics* (1970–1991), and *Journal of Applied Physics* and *Applied Physics Letters* (1978–1980).

Dr. Holonyak received a General Electric Cordiner Award (1962), and for his contributions to the field of visible-spectrum light emitting diodes and diode lasers, he is the recipient of the IEEE Morris N. Liebmann Award (1973), the John Scott Medal (1975, City of Philadelphia, PA), the GaAs Symposium Award with Welker Medal (1976), the IEEE Jack A. Morton Award (1981), the Electrochemical Society Solid State Science and Technology Award (1983), the Sigma Xi Monie A. Ferst Award (1988), the IEEE Edison Medal (1989), the Charles Hard Townes Award of the Optical Society of America (1992), the National Academy of Sciences Award for the Industrial Application of Science (1993), American Electronics Association 50th Anniversary Award (1993, "Inventing America's Future"), American Society for Engineering Education Centennial Medallion (1993), Vladimir Karapetoff Eminent Members' Award of Eta Kappa Nu (1994), and 1995 TMS John Bardeen Award (The Minerals, Metals, and Materials Society). In 1990, he received the U.S. National Medal of Science, and in 1992 received from Northwestern University an Honorary Doctor of Science degree and was elected an honorary member of the Ioffe Physical-Technical Institute (St. Petersburg, Russia). In 1994, he received an Honorary Doctor of Engineering degree from Notre Dame University, and in 1995 received the Japan Prize. In 1993, he was appointed (University of Illinois) the John Bardeen Chair Professor of Electrical and Computer Engineering and of Physics, a chair sponsored by the Sony Corporation. He is a member of the National Academy of Engineering (1973), National Academy of Sciences (1984), Fellow of the American Academy of Arts and Sciences (1984), the American Physical Society, and the Optical Society of America.