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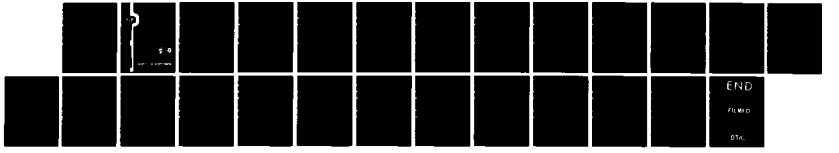

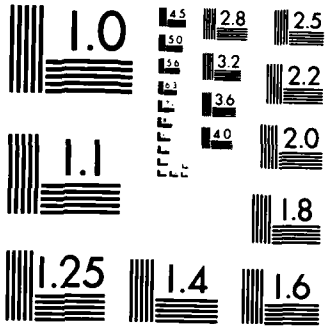

Research on GaSb/AlSb
Multi-Quantum Well Superlattices
Final Report on
ONR Contract N00014-76-C-1044

by Herbert Kroemer
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All growths took place on GaAs substrates, with an AlSb buffer layer between the substrate and the superlattice. Despite the very large lattice mismatch (>7%) between GaAs and GaSb/AlSb, it was found that only the first few wells of the superlattice appeared somewhat defective, and that the superlattice growth itself very effectively suppressed the propagation of misfit dislocation and of other structural and morphological defects from the substrate/buffer layer interface into the superlattice portion of the epilayer. Although the defect-suppressing effect of superlattice growth had been observed before, this is by far the most extreme case for which it was found highly effective; it suggests that MBE growth, if conducted with superlattice buffer layers, offers far more fredom in the nature and quality of the substrate than has heretofore been thought.

From the photoluminescence data it was concluded that the Γ-valley of the GaSb band structure gets pushed above the L-valleys for well widths below 3.8nm, rather than already below 9nm, as was previously thought. For well widths below the direct-to-indirect crossover, the direct-gap luminescence dropped in intensity by over two orders of magnitude, but remained visible down to the narrowest wells studied, with a strength comparable to the (presumably phonon-assisted) weak indirect-gap luminescence originating from the lower L-valleys themselves, which was also clearly observed.

The photoluminescence decay times of the direct-gap luminescence increased from less than 1ns in the direct-gap range to about 100ns in the indirect-gap range, indicating that the direct-gap luminescence in the indirect-gap range cannot be due to primary electrons initially captured by the Γ-valley and surviving there, but must be due to electrons from the lower L-valleys somehow being lifted back up into the Γ-valley. The energies and temperatures involved rule out a thermal re-excitation process, and suggest an Auger-like process, but the details of the latter remain obscure.

The indirect-gap luminescence from the L-valleys overlapped with a broad luminescence band at lower energies, the origin of which could be traced to the defective wells near the interface betwen the superlattice and the AlSb buffer layer. It was absent in the remainder of the superlattice.

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on

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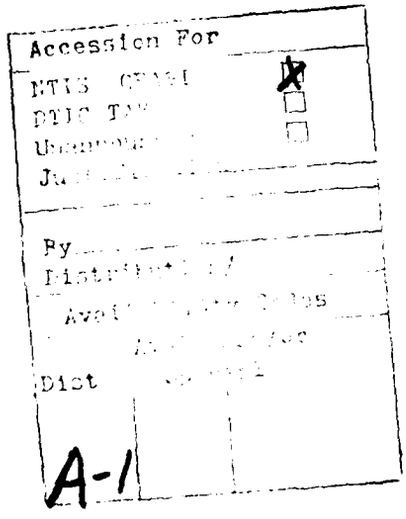
Santa Barbara, CA 93106

Note: This Final Report was delayed because we were still awaiting valuable test results from samples prepared under this contract, and turned over to Dr. Forchel of the Physics Department of the University of Stuttgart, Germany. Because much of the final evaluation of the research under this contract hinged on these test results, we felt it was essential that these data be included. These data, which have now been received, form an essential part of this Final Report.



Research on GaSb/AlSb Multi-Quantum Well Superlattices

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Abstract

Multi-quantum-well GaSb/AlSb superlattices (SLs) with well widths ranging from 12nm down to 1.2nm were grown by molecular beam epitaxy (MBE), and their photoluminescence (PL) properties were studied.

All growths took place on GaAs substrates, with an AlSb buffer layer between the substrate and the superlattice. Despite the very large lattice mismatch (>7%) between GaAs and GaSb/AlSb, it was found that only the first few wells of the superlattice appeared somewhat defective, and that the superlattice growth itself very effectively suppressed the propagation of misfit dislocation and of other structural and morphological defects from the substrate/buffer layer interface into the superlattice portion of the epilayer. Although the defect-suppressing effect of superlattice growth had been observed before, this is by far the most extreme case for which it was found highly effective; it suggests that MBE growth, if conducted with superlattice buffer layers, offers far more fredom in the nature and quality of the substrate than has heretofore been thought.

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Introduction: The Background

The research conducted under this contract over a number of years concerned itself with various new properties of semiconductor heterostructures, especially with various aspects of new and unconventional forms of light emission from semiconductors. An early topic -- starting in 1978 -- was the search for recombination radiation in indirect-gap semiconductors under conditions of high-level injection. The initial idea was that two electrons from opposite valleys in the Brillouin zone would recombine with two holes in the valence band under the emission of a single photon with twice the gap energy. Such an effect had been observed in Si by workers at the University of Stuttgart [1]. The effect had been very weak, but this was to be expected: The intensity of such an effect should be proportional to $(np)^2$, where n and p are the electron and hole concentrations. Such a steep dependence means that the effect will be very weak for low minority carrier concentrations, but it should increase drastically with increasing excitation, especially if the minority carrier concentration could be raised far above the doping level, because in this case the majority carrier concentration would increase as well. The test structures used by the Stuttgart group were essentially pieces of bulk silicon, in which the minority carriers were not confined, and hence could not accumulate to a high concentration. To achieve a high intensity calls for an electron- and hole-confining structure like a double-heterostructure laser, and considering the very steep dependence of the effect on concentration, a drastic increase of intensity might in fact be expected. We concluded that a GaAs/Ge/GaAs double heterostructure offered the best chance for observing a strong effect. In it very high population inversions could presumably be achieved. In addition, the energy band structure of Ge is much more favorable than that of Si. We were just in the process of acquiring MBE equipment for the growth of GaP on Si, under ARO sponsorship, and simultaneous work on GaAs-on-Ge and Ge-on-GaAs heterostructures appeared to form a potentially synergistic complement to the GaP-on-Si work, being benefitted by the latter, and benefitting it in return.

In 1979, an additional possibility for light emission and even laser action in indirect-gap semiconductors emerged, when Holonyak's research group at the University of Illinois reported certain peculiar spectral features in GaAs/(Al,Ga)As multi-quantum-well lasers, for which the least implausible interpretation was phonon-assisted laser action, with a strong suggestion that the phonon emission was itself stimulated [2]. Inasmuch as GaAs is a direct-gap semiconductor, it should not require phonon assistance for laser action. A theoretical analysis, performed under this contract and subsequently published [3], identified the conditions that must be met for such doubly-stimulated emission (DSE) to occur, and the results appeared sufficiently promising to pursue further. In particular, IF the interpretation of the Illinois data in terms of DSE was indeed correct, which appeared likely, then phonon-assisted laser action should be possible to achieve in a suitable indirect-gap semiconductor, like Ge. Again the most promising structure to build for a test appeared to be a GaAs/Ge/GaAs double heterostructure.

The GaAs-on-Ge system seemed initially much easier than the GaP-on-Si system, and some of our first results of growing GaAs on Ge, using the unconventional crystallographic (110) orientation [4], appeared exceptionally promising. Research on both

the GaAs-on-Ge and the GaP-on-Si systems clearly would be mutually supporting. We decided to pursue both systems in parallel, GaP-on-Si under ARO sponsorship, GaAs-on-Ge under this ONR contract. We embarked on an extended effort to grow GaAs/Ge/GaAs double heterostructures. The research made significant contributions to the understanding of the problems involved in growing polar compound semiconductors like GaAs or GaP on non-polar elemental substrates like Ge or Si, leading ultimately to a Ph.D. dissertation for Gerard Sullivan [5]. Unfortunately, the outcome of this research with respect to the *specific* needs of GaAs/Ge/GaAs double heterostructures was largely negative: Device-quality GaAs-on-Ge interfaces, as they would be necessary for high-level injection structures, appear to be unachievable.

Although the GaP-on-Si and the GaAs-on-Ge system did have many things in common, they were far more different than we -- or anyone else -- had expected. In particular, it turned out quite unexpectedly that GaAs-on-Ge was the more difficult one of the two systems, and GaP-on-Si the easier one. In the course of protracted and very frustrating experimentation it gradually emerged [5] that the reason for the difficulty with GaAs-on-Ge is an incompatibility of temperature ranges: GaAs does not grow with acceptable quality below about 500^{0}C, but at that temperature it already reacts noticeably with the Ge substrate, leading to an unacceptable concentration of interface defects, not to mention the Ge uptake and hence heavy doping in the GaAs itself. To keep the reaction with the Ge surface negligible, the GaAs growth temperature had to be lowered to about 400^{0}C, which is hopelessly too low for good GaAs growth. Symptomatic of these difficulties, we were never able to achieve even mediocre reverse characteristics for GaAs-on-Ge heterojunctions, nor any trace of any minority carrier injection under forward bias [5].

By contrast, in the case of GaP-on-Si growth, we found a temperature range about 30^{0}C wide (550^{0}C - 580^{0}C) over which GaP-on-Si interfaces could be achieved that were sufficiently good that they could be used as emitter interfaces in a (mediocre but working) GaP-on-Si heterostructure bipolar transistor, and the reverse characteristics of those junctions were in fact excellent [6].

Our experiences with the GaAs-on-Ge growth make us take an extraordinarily dim view of numerous recent claims that good growth of GaAs on Si can be achieved by first depositing Ge on the Si surface, or that such a Ge interlayer might in fact be necessary. The majority of papers on GaAs-on-Si growth employed Ge inter-layers (some even involved straight growth on Ge), but the originators of the Ge interlayer approach have themselves declared this to be unnecessary [7], in contrast to their earlier claims. It appears that the only useful purpose of the Ge layer was to cover up the oxide contamination on the Si surface. At UCSB we take the point of view that Ge is actually harmful to good growth, because the amount of Ge taken up by the growing GaAs and doping it, is believed to be much larger than the amount of Si taken up from a Si substrate.

It was the difficulties and failures of the GaAs-on-Ge system that eventually led us naturally to the GaSb/AlSb heterosystem, which occupied us for the last three years of this contract, and with which the balance of this Final Report is concerned.

The GaSb/AlSb Heterosystem

It had been clear from the outset that a possible alternative to GaAs/Ge would be one of the indirect-gap III/V compounds, lattice-matched to another III/V compound. When it became clear that the GaAs/Ge was unlikely to be technologically successful, the work was shifted in that direction. There were two choices. The most obvious system would be an all-(Al,Ga)As system, with two different Al:Ga ratios, both above 50:50. The other system was the GaSb/AlSb quantum well system. Although GaSb is a direct-gap semiconductor, the L-valleys in GaSb are only about 80 mev above the Γ-valleys, and in a sufficiently narrow quantum well (we estimated for < 90Å) they should get pushed above the L-valleys, making the gap indirect [8].

We considered both the all-(Al,Ga)As combinations and the GaSb/AlSb system, and concluded that GaSb/AlSb, although less obvious, was far more promising. Both fundamental and technological reasons entered this judgement.

The fundamental reason was this: It was clear from Holonyak's model of phonon-assisted laser action [2], as well as from our own theoretical analysis [3], that only sufficiently deep quantum wells would create the number of *spontaneously* emitted optical phonons necessary to get the stimulated emission started. From the then-accepted band lineups in the (Al,Ga)As system [9] it appeared that indirect-gap quantum wells in that system would be undesirably shallow. It has become clear since then that the band lineups are even less favorable [10], thus further justifying our choice. By contrast, the wells in the GaSb/AlSb system are almost certainly amongst the deepest wells possible, perhaps as deep as 1.4 eV [8].

Technologically, it was already well-known at that time that (Al,Ga)As alloys with a high Al fraction are very prone to form semi-insulating material dominated by deep levels, hardly a desirable state of affairs inside a laser cavity. In the GaSb/AlSb system only the less-critical barriers separating the GaSb wells would contain Al; the wells themselves, which are more critical, are pure GaSb, expected to be easy to grow. Finally, the idea of working with two binary compounds rather than with two ternary alloys, was very appealing. It would be possible to study the direct-to-indirect gap transition by simply varying the width of the wells rather than the composition of an alloy.

Growth of GaSb/AlSb Superlattices: The Morphology Breakthrough.

The GaSb/AlSb superlattice system turned out to be even easier to grow than we had expected. We had taken it for granted that a lattice-matched substrate would be necessary, and inasmuch as AlSb is not commercially available at all, the natural choice would have been GaSb, with InAs being a remote alternate choice. The only commercial source of substrate material was Sumitomo in Japan, with long delivery times (and very high prices). Rather than wait for substrate deliveries, we simply performed the first growth experiments on GaAs substrates, despite the huge lattice mismatch (>7%). These inital experiments showed quickly that the morphology of both GaSb and AlSb on this badly mismatched

substrate, although not satisfactory for high-quality layers, was good enough to suggest that much of the "roughing-in" of the growth technology could be worked out using GaAs substrates, with the need for GaSb substrates anticipated only for "fine tuning". A next unexpected observation was that the morphology of AlSb grown on GaAs was significantly better than that of GaSb on GaAs, and that the growth of GaSb on GaAs could be improved considerably by first growing a thin AlSb buffer layer on the GaAs substrate. Finally, we discovered that the morphology of GaSb/AlSb superlattices was *drastically* better than that of "bulk-type" non-superlattice layers, to the point that it approached the morphology of high-quality GaAs/(Al,Ga)As growth! Photoluminescence measurements confirmed the high quality of the superlattice layers. It was a major breakthrough, which drastically changed the subsequent course of the research.

Our own work was not without precedent; the topic was "in the air": Chai and Chow [11] had just demonstrated that surprisingly large lattice mismatches can be accommodated by superlattice buffer layers without the propagation of dislocations into the epilayers. What happens is that the growth of the superlattice itself suppresses the propagation of misfit dislocations from the mismatched hetero-interface into the epilayer. However, the lattice-mismatched layers grown by them, while improved, were far from satisfactory for our needs. It was subsequently shown by Petroff et al. [12] that in well lattice-matched (Al,Ga)As/GaAs growth, superlattice buffers not only suppress dislocations, but improve both the morphology in general, along with the photoluminescence properties of epitaxial layers grown over them.

We were aware of this work of others, and it probably influenced us towards simply trying superlattices on GaAs substrates, lattice-matched or not. However, the full magnitude of the improvement under our extreme circumstances could not have been predicted from that earlier work. Ours is by far the most extreme case for which the defect-suppressing effect of superlattice growth was found highly effective; it suggests that MBE growth, if conducted with superlattice buffer layers, offers far more fredom in the nature and quality of the substrate than has heretofore been thought. This would be far-reaching indeed. Having significantly contributed to this development may be one of the major hidden contributions made by the research under this contract.

The idea that the quality of MBE growth can be drastically improved by the incorporation of superlattice buffer layers [12],[13] became widely accepted during 1984, and some of the more advanced research groups are now tending towards incorporating superlattice buffers routinely in their growths unless there is a specific reason *not* to do so. We ourselves have just completed a project on the MBE growth of GaAs on Si [14], in which the use of a superlattice buffer made it possible to obtain much higher-quality growth, with much better morphology, than without such a buffer layer. Another application has been the use of superlattice buffers to obtain good growth on crystallographic orientations that do not polish well: We have obtained excellent growth of GaAs layers and (Al,GA)As superlattices on the (211)A orientation [15], even though the (211)A wafers polish poorly, similar to (111)A wafers.

Photoluminescence

We grew a series of GaSb/AlSb superlattices with well widths from 12nm down to 1.2nm, and we performed extensive low-temperature photoluminescence measurements on these structures. The principal results of this effort have been published [8]. A reprint of this publication is attached, to which we would like to refer for details. In the present report we shall go directly to some re-interpretations of the results, and to the implications of the entire research with regard to the original motivation for this work, phonon-assisted laser action in indirect-gap semiconductors, something (deliberately) omitted from the paper.

In our work we had found that recombination radiation attributed to the direct-gap transition could be observed down to the narrowest quantum wells studied (1.2nm), at which point the lowest-energy states inside the GaSb wells should no longer be the direct-gap Γ-valley states, but either L-valley states or -- more likely -- X-valley states. However, the intensity of that radiation dropped precipitously, by about a factor 1:300, when the well width was reduced from about 5nm to about 3nm, with most of the drop taking place between 3 and 4nm. We attributed this drop to the onset of competition from the X-valleys, which were expected to cross the Γ-valleys slightly below that well width. But we also expressed our surprise about the absence of any evidence for the competition with the L-valleys, which should have occurred already slightly below 9nm, in a region where the direct-gap photoluminescence was in fact strongest. We believe today that the resolution of this puzzle is that the L-valleys do in fact not cross over below the Γ-valley until much lower well widths, and that the precipitous drop of the direct-gap luminescence is due to the onset of competition from the L-valleys rather than the X-valleys. This interpretation is in conflict with what is known about the *unstrained* band structure of GaSb; the only way we can offer to resolve the discrepancy is to postulate that the considerable strain present in the GaSb/AlSb system (0.6%) shifts the Γ-valleys downwards relative to the L-valleys by an amount sufficiently large that the band crossover is shifted to thinner quantum wells. This is admittedly an ad-hoc hypothesis, but the other alternative would be a very large electron population in the L-valleys that does not manifest itself in any way whatsoever, an implausible proposition.

For those layers with quantum well widths below the crossover width, we found a second very broad luminescence band, for which we attempted an exotic explanation, which we have since then abandoned in favor of a much simpler explanation that grew out of photoluminescence work on our samples done at Stuttgart University in Germany, much of it after the formal expiration of this contract.

Photoluminescence Work at Stuttgart

During May and June 1984, the PI spent two months of a sabbatical at Stuttgart University, in Prof. Pilkuhn's laboratory. The choice had been influenced at least partially by the continuing role of the Stuttgart laboratory as one of the leading laboratories in the field of radiative emission from semiconductors. Dr. Forchel of Prof. Pilkuhn's laboratory expressed a strong interest in cooperating with the PI, by performing various

measurements beyond our own capability on our samples. We provided him first with a few selected samples to perform time-resolved photoluminescence, and after these measurements yielded a surprising amount of new information, we turned over the remainder of our samples to him, for an in-depth study. In addition to checking (and confirming) our own Argon-laser-excited photoluminescence data, the following studies were performed:

(a) Dependence of photoluminescence spectra on excitation wavelength (excitation spectroscopy), using a tunable dye laser, to obtain depth information about the *spatial* origin of the different portions of the photoluminescence spectrum.

(b) Time-resolved photoluminescence, following excitation by 150 ps pulses, from an Argon laser with cavity dumper and mode locker, using a fast S1 photomultiplier, with an overall time resolution of about 300 ps.

(c) Study of intensity ratio of the direct-gap to indirect-gap luminescence for several indirect-gap samples, as a function of the excitation intensity, over an excitation range up to 400:1 wide.

(d) Study of the temperature dependence of the photoluminescence spectra, for the two indirect-gap samples for which the direct gap was closest to the indirect gap.

The different measurements provided a wealth of new information, and they resolved many questions. Manuscripts for two joint Stuttgart-Santa Barbara papers on these measurements are in preparation, one for a short Physical Review Letters paper, another for a full-length paper; a third paper on additional measurements still in progress may follow. Copies of the final submission manuscripts, and of reprints after publication, will be forwarded to ONR, as usual. In the remainder of the present report, we are summarizing the results of the Stuttgart work, together with the important conclusions that follow from it.

Most notable was a resolution of the puzzle about the origin of the very broad emission band between 0.8 eV and 1.2 eV, seen in all our indirect-gap samples. The depth resolution provided by the measurements under (a) above showed this band to consist of two smmothly overlapping parts of completely different origin: The portion below about 1.0 eV originated from near the interface between the GaSb/AlSb superlattice and the AlSb buffer layer, whereas the portion above about 1.0 eV is true indirect-gap photoluminescence, presumably phonon-assisted, originating from the L-valleys inside the GaSb layers of the superlattice itself. This split origin was not at all apparent from our own data, and its discovery was a major surprise. However, once this dual origin had been recognized, many previously mysterious aspects of our observations fell into place.

The lower-energy portion of the broad radiation band, having been identified as coming from near the interface, appears to have a very simple explanation: It is almost certainly due to local thickness fluctuations in the first few GaSb layers of the superlattice, caused by a less-than-perfect morphology of the 200 nm thick AlSb buffer layer on top of the lattice-mismatched GaAs substrate. In the case of (Al,Ga)As growth it is by now well-known

that the morphology of (Al,Ga)As layers tends to degrade with increasing thickness [16], and one should expect the same for AlSb, probably aggravated by the lattice-mismatched substrate. The first few periods of of a superlattice very quickly smooth out these features, leading to the superb morphological quality of the upper portions of the superlattice, but leaving the lowermost layers with an uneven thickness. In those portions of the lowermost layers that have an above-average thickness, the electrons will then be less strongly quantized, which leads to photon energies shifted down, towards the bulk energy gap of GaSb. Inasmuch as the thickest portions of the first few layers have the narrowest effective energy gap, there is actually an effective potential gradient driving the electron-hole pairs towards those portions, increasing the contributions of the latter to the total radiation. Finally, the contribution of the first few GaSb layers to the total radiation is enhanced by the fact that these layers act as a sink for any electron-hole pairs generated within the AlSb buffer layer.

We had, in fact, considered earlier the possibility that the broad low-energy band might be due to GaSb layers of excessive thickness, but had rejected this explanation because it could not plausibly explain the full width of this band. Once it was recognized that the band is of composite origin, this objection disappeared.

The higher-energy portion of the broad band also now has a simple natural explanation: It is almost certainly "ordinary" phonon-assisted emission from electrons in the L-valleys rather than the exotic two-electron process involving electrons from two opposite X-valleys postulated earlier. Although the latter concept had explained the *entire* broad low-energy band, it had failed to explain why the L-valleys were apparently not visible at all, and hence there was always a strong air of implausibility about that "X-hypothesis".

The acceptance of the idea that it is the L-valleys rather than the X-valleys that cross over the Γ-valleys around a well width of 3.8 nm, comes at a price: There is no way how a crossover at any well width below about 6 nm can be explained from the *unstrained* bulk band structures, and one is forced to the ad-hoc assumption that the large uniaxial strains in the poorly lattice-matched GaSb/AlSb system (0.6% lattice mismatch) causes a large increase in the separation between the Γ- and L-valleys. However, this appears to be a less implausible assumption than that of an essentially invisible heavily populated L-valley.

The time-resolved photoluminescence measurements of the Stuttgart group showed clearly that the persistent but greatly weakened *direct-gap* luminescence below 3.8 nm well width is not due to "primary" electrons captured into the Γ-valley, but due to electronic collected into the lower-lying L-valleys, which *somehow* found their way back up into the Γ-valley, from where they recombined radiatively: The time constant for the decay of the direct-gap luminescence from the indirect-gap superlattices was over two orders of magnitude longer (≈ 100ns) than in the direct-gap superlattices (< 1ns). A consideration of the energy differences between the valleys involved, showed that at least at low temperatures (2K) the process of lifting electrons from the L-valleys to the Γ-valley could not possibly be a thermal process, but had to be some "Auger-like" process, in which two electrons are involved, one falling into the valence band, transferring its energy to a second electron, which thereby gets kicked up high into the Γ-valley, from where it may either recombine radiatively or -- more likely -- get scattered back into the L-valley. The simplest

form of any such model (assuming pure band-to-band Auger transitions, not involving defects), predicts that the ratio of Auger-assisted direct-gap recombination to phonon-assisted indirect-gap recombination should increase strongly with increasing pump intensity. However, the Stuttgart measurements show clearly an essentially excitation-independent intensity ratio. This suggests that the postulated "Auger-like" process somehow involves transitions at defects. The details remain obscure, but it is gratifying to note that our original idea of a two-electron process, while significantly modified, survives in this modified form.

Conclusions

To the extent that an explicit goal of this research was to search for *intense* phonon-assisted radiative recombination in an indirect-gap semiconductor, preferably even laser action, this goal appears unachievable. Although some phonon-assisted luminescence was found, from the L-valleys in the GaSb/AlSb superlattice system, the effect is much too weak to offer any realistic chance for phonon-assisted laser action. But if phonon-assisted laser action does not occur in an *indirect-gap* structure such as this, it is hard to accept that the effects observed by Holonyak et al. are indeed due to doubly-stimulated emission. Hence the question as to the exact mechanism of the effects seen by that group remains as wide-open as ever.

Although failing in its *declared* objective, the research had a very large amount of highly beneficial "fallout": The study of the GaSb/AlSb superlattice can stand on its own, as the most detailed study of any superlattice other than GaAs/(Al,Ga)As, with significantly different properties, and, by complementing GaAs/(Al,Ga)As, significantly enhancing our understanding of superlattices in general.

Much of the fallout was technological, almost all of that unexpected. Our work demonstrated, far beyond anything demonstrated before, or even suspected, that superlattices make it possible to achieve epitaxial growth on very badly lattice-mismatched substrates, yet with properties as good as the best bulk growth. This is a breakthrough in epitaxial technology as such.

Even the work on the GaAs/Ge system, although superficially a disaster, had some benefits: It helped significantly with the simultaneous GaP-on-Si work, and thereby contributed indirectly to the current promising developments in GaAs-on-Si technology. And if it prevents others from wasting time and resources on further fruitless efforts towards device-quality GaAs-on-Ge growth itself, our own failures will not have been totally in vain.

References

Note: References [3], [4], [5], and [8] represent work supported partially or entirely by this contract. Except for reference [5], reprints are attached to this report.

[1] See, for example, K. Betzler, W. Weller, and R. Conradt, Phys. Rev. B **6**, 1394 (1972), where references to earlier work are given.

[2] For a review through late 1979 see N. Holonyak, Jr. R. M. Kolbas, R. D. Dupuis, and P. D. Dapkus, IEEE J. Quantum Electron. **QE-16**, 170 (1980); for some subsequent work, see: (a) J. J. Coleman, P. D. Dapkus, B. A. Vojak, W. D. Laidig, N. Holonyak, Jr., and K. Hess, Appl. Phys. Lett. **37**, 15 (1980); (b) N. Holonyak jr., B. A. Vojak, W. D. Laidig, K. Hess, J. J. Coleman, and P. D. Dapkus, Appl. Phys. Lett. **37**, 136 (1980).

[3] H. Kroemer, Appl. Phys. Lett. **38**, 959 (1981). This paper represents work supported by this contract. A reprint is attached to this report.

[4] H. Kroemer, K. J. Polasko, and S. L. Wright, Appl. Phys. Lett. **36**, 763 (1980). This paper represents work supported in part by this contract. A reprint is attached to this report.

[5] G. S. Sullivan, Dissertation, University of California, Santa Barbara, 1983, unpublished. This work was supported by this contract.

[6] S. L. Wright, H. Kroemer, and M. Inada, J. Appl. Phys. **55**(#8), 2916-2927, April 1984.

[7] B. Y. Tsaur and G. M. Metze, Appl. Phys. Lett. **45**, 535 (1984). See this paper also for some key references to earlier work on this topic, not cited here.

[8] For details and backup references see: G. Griffiths, K. Mohammed, S. Subbanna, H. Kroemer, and J. L. Merz, Appl. Phys. Lett. **43**,1059 (1983). This paper represents work supported by this contract. A reprint is attached to this report.

[9] For a compact review of the theoretical status at that time, see H. Kroemer, J. Vac. Sci. Technol. B **2**, 433 (1984), where detailed references to the original work are given.

[10] The number of papers on this topic is large and growing, and it does not appear to be useful to give a full bibliography. We give here only the first four papers of this development: (a) R. C. Miller, A. C. Gossard, D. A. Kleinman, and O. Munteanu, Phys. Rev. B **29**, 3740 (1984); R. C. Miller, D. A. Kleinman, and A. C. Gossard, Phys. Rev. B **29**, 7085 (1984); (b) W. I. Wang, E. E. Mendez, and F. Stern, Appl. Phys. Lett. **45**, 639 (1984). (c) M. O. Watanabe, J. Yoshida, M. Mashita, T.

Nakanisi, and A. Hojo, Intl. Conf. Solid-State Dev. & Matls., Kobe 1984; (d) S. Tiwari and W. I. Wang, IEEE Elect. Dev. Lett. **EDL-5**, 333 (1984).

[11] Y. G. Chai and R. Chow, J. Appl. Phys. **53**, 1229 (1982).

[12] P. M. Petroff, R. C. Miller, A. C. Gossard and W. Wiegmann, Appl. Phys. Lett. **44**, 217 (1984).

[13] D. Arnold, W. Kopp, R. Fischer, T. Henderson, and H. Morkoc, IEEE Elect. Dev. Lett. **EDL-5**, 82 (1984); R. Fischer, J. Klemm, W. Kopp, and H. Morkoc, Appl. Phys. Lett. **44**,1 (1984); W. T. Masselink, M. V. Klein, Y. L. Sun, Y. C. Chang, R. Fischer, T. J. Drummond, and H. Morkoc, Appl. Phys. Lett. **44**, 435 (1984).

[14] P. N. Uppal and H. Kroemer, J. Appl. Phys., in the press.

[15] S. Subbanna, H. Kroemer, and J. L. Merz, to be published.

[16] See, for example: R. C. Miller, W. T. Tsang, and O. Munteanu, Appl. Phys. Lett. **41**, 374 (1982).

GaSb/AlSb multiquantum well structures: Molecular beam epitaxial growth and narrow-well photoluminescence

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Multiquantum well structures of GaSb wells down to 12-Å width, separated by 120-Å AlSb barriers, were grown by molecular beam epitaxy, and their low-temperature photoluminescence was studied. Even though GaSb should become an indirect-gap semiconductor for well widths below about 90 Å, the direct-gap luminescence persists to the narrowest wells. The shift of photon energy with well width indicates strong nonparabolicity effects; it is in good agreement with Bastard's simple model of quantum wells in nonparabolic semiconductors. For wells less than 45 Å wide, the direct-gap luminescence is accompanied by a strong and very broad lower-energy luminescence peak, which appears to be related to electron accumulation in the X valleys, but the exact mechanism for which is not clear. A two-electron transition model is proposed.

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In contrast to the wealth of studies on GaAs/(Al, Ga) As quantum well structures, only very few reports on quantum well structures in the GaSb/AlSb heterosystem have so far been published.[1-4] Although qualitatively similar to GaAs/AlAs, GaSb/AlSb exhibits major quantitative differences.

The gap difference between the two semiconductors in the GaSb/AlSb system is much larger relative to the narrower-gap semiconductor (GaSb) than in the GaAs/AlAs system[5]: $\Delta\epsilon_g(\Gamma\text{-to-}X) \sim 0.86$ eV $\sim 1.19\epsilon_g$(GaSb); $\Delta\epsilon_g(\Gamma\text{-to-}\Gamma) \sim 1.50$ eV $\sim 2.06\epsilon_g$(GaSb). (All data are for 300 K.) For the GaAs/AlAs system the two ratios are only 0.52 and 1.12. Because of the common-anion rule [6-8] of band lineups, the valence-band offset at a GaSb/AlSb heterojunction should be small; the Harrison theory[8] predicts essentially zero valence-band offset. Hence, GaSb/AlSb electron quantum wells should be deep, with significant deviations from the simple model of a single parabolic band.

GaSb is only barely a direct-gap semiconductor. The L valleys are only 0.07 eV, the X valleys only about 0.29 eV above the Γ valley. Because of the low effective mass in the Γ valley (0.042 m_e), confining the electrons in a sufficiently narrow quantum well will quickly push the Γ valley above the L valleys and eventually above the X valleys. If, to the first order, one treats the wells as infinitely deep and neglects nonparabolicity effects, one estimates a Γ/L crossover around 99-Å well width[9] and a Γ/X crossover around 53 Å. The actual crossovers should occur at somewhat narrower wells, especially the Γ/X crossover.

The change in room-temperature photoluminescence (PL) with GaSb well width, under relatively weak excitation by a He-Ne laser, has already been studied by Naganuma *et al.*,[1] who reported that the direct-gap (Γ) luminescence persisted past the Γ/L crossover point, although with steeply decreasing intensity. We report here PL observations on GaSb multiquantum well structures taken at 1.6 K under much more intense excitation (Ar^+ laser, 4880 Å, $\gtrsim 10^4$ W cm^{-2}), and extending to narrower wells down to 12 Å. We find (Fig. 1) that the direct-gap luminescence persists with apparently undiminished intensity down to well widths of ~ 50 Å. Between 50 and 30 Å the intensity drops steeply by a factor of about 300, but persists at that diminished strength down to the narrowest wells studied. The dependence of quantum energy on well width exhibits strong nonparabolicity effects (Fig. 2). For well widths below ~ 45 Å, the Γ luminescence is accompanied by a very broad lower-energy luninescence, which for wells below 35 Å contains a *much larger integrated intensity than the Γ peak* (Fig. 3).

The quantum well structures were grown on GaAs (100) substrates in a Varian MBE 360 system. The substrates were cleaned, etched, mounted, and heat cleaned as for the homoepitaxial MBE growth of GaAs, followed by the growth of a 2000-Å AlSb buffer layer. Despite the large lat-

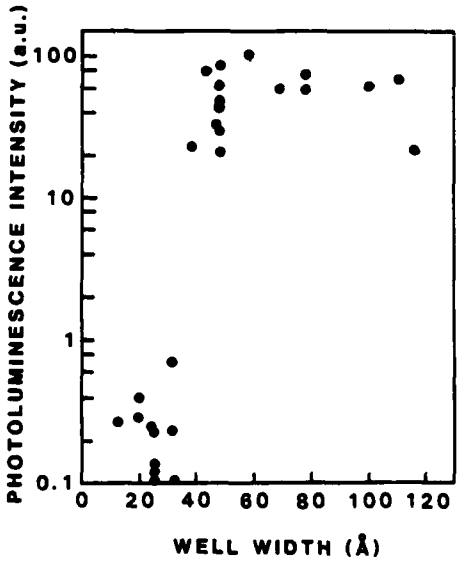

FIG. 1. Intensity of 1.6-K direct-gap photoluminescence of GaSb/AlSb multiquantum well structures, as a function of well width. The radiation was excited using an Ar^+ laser ($\sim 10^4$ W cm^{-2}) and detected with a Ge detector cooled to 77 K.

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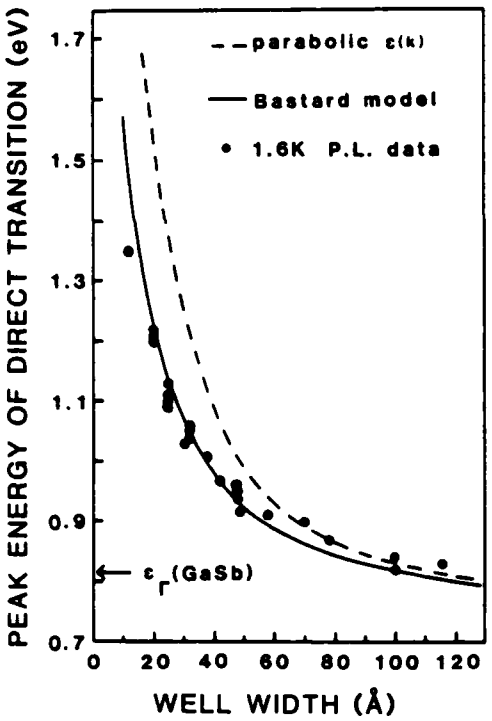

FIG. 2. Photon energy of direct-gap photoluminescence, as a function of well width. The solid curve shows a theoretical fit to Bastard's model (see Ref. 12) of energy levels in semiconductor quantum wells, including nonparabolicity effects in the band structure. The fit to a parabolic $\epsilon(k)$ model is also shown.

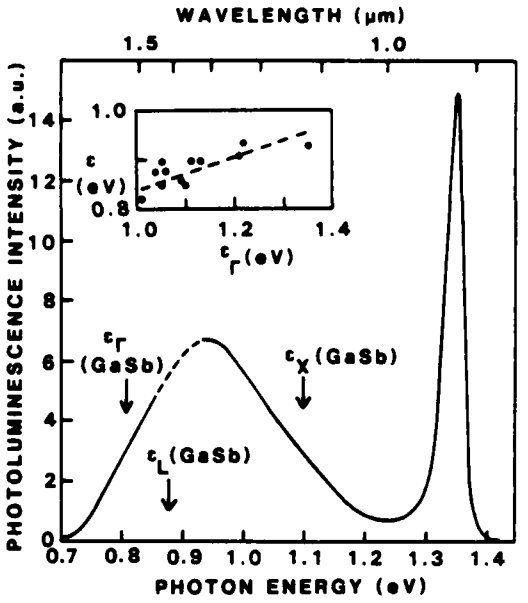

FIG 3. Photoluminescence spectrum at 1.6-K of GaSb/AlSb multiquantum well structure with 12-Å well widths, showing a relatively sharp Γ peak at ~1.35 eV and a much broader peak around 0.95 eV. Both peaks shift to lower energies as the well width is increased, but the low-energy peak shifts much less rapidly than the Γ peak, as shown in the inset. The spectrum has been corrected for the response function of the apparatus.

tice mismatch between AlSb and GaAs (~8%), smooth epitaxy resulted after less than 20 monolayers, with reflection high-energy diffraction (RHEED) patterns comprising long unmodulated (3 × 1) streaks. The best patterns were obtained for nucleation at 560 °C.

The subsequent superlattices were grown at a lower temperature. The effect of growth temperature and flux ratio on the array PL was investigated for substrate temperatures between 450 and 530 °C, and for atomic flux ratios Sb:Ga and Sb:Al between 1.4 and 3.5. The best PL was observed for the higher temperatures and a flux ratio of ~2.0; the dependence on flux ratio was weak. The (not intentionally doped) GaSb and AlSb were both *p*-type, with hole concentrations around 5×10^{16} cm^{-3}, presumably due to the native acceptor commonly found in GaSb, independent of growth technology.

All but one quantum well array consisted of 120-Å barriers separating GaSb wells of various thicknesses. The surface morphology of the superlattices appeared distinctly better (both visually and by RHEED) than that of straight GaSb or AlSb. Apparently, the first few periods of the slightly strained GaSb/AlSb arrays act as dislocation barriers,[10,11] leading to subsequent growth of higher perfection (and presumably more perfect interfaces) than might otherwise be the case. The total array thickness was kept constant at 1 μm, large compared to the estimated penetration depth of the pump light (0.1–0.3 μm), and restricting the excitation to the structurally most perfect part of the array. Thus, the number of quantum wells varied, from 76 for the 12-Å wells, to 42 for the 120-Å wells. Two samples were grown with 25-Å wells, and with barrier widths of 60 and 120 Å, respectively. Only very small shifts (≲0.03 eV) in the resulting PL spectra were observed, indicating that the individual wells are fully decoupled at 120 Å.

Both the well widths and the barrier thicknesses were controlled by accurate monitoring of the Ga and Al fluxes using a nude ion gauge beam flux monitor, which in turn had been calibrated by growing thick (> 2 μm) GaSb and AlSb layers and measuring their thicknesses interferometrically. The growth rates for both materials were maintained at 1 Å/s for all samples, at the center of the substrate. To minimize sample thickness errors due to the (11%) growth rate gradient across the substrates, caused by an oblique Ga beam, the PL samples were cleaved from near the center of the substrate. The principal source of thickness uncertainties are probably fluctuations in the run-to-run reproducibility of the Ga flux itself. The variations amongst the four 48-Å runs shown in Fig. 2 suggest beam flux reproducibility fluctuations of about ± 10%. For the narrower wells, the resulting well width variations are below the inevitable atomic-scale roughness in the heterointerface itself.

The structures were capped with a 300-Å layer of AlSb followed by a 1000-Å layer of epitaxial Al grown at room temperature. The purpose of the Al layer was to facilitate electrical measurements and to protect the structure during sample preparation for PL measurements.

The samples were prepared for PL by cleaving 2-mm square sections which were then indium-soldered to a glass strip for insertion into the cryostat. Once mounted, the Al coating was removed by selectively etching in 10% KOH. The exposed surface immediately developed an oxide layer, but remained stable in dry air.

Figure 2 shows the energies of the 1.6-K Γ-peaks of the

PL spectra as a function of the nominal GaSb well width, for all samples on which PL spectra were taken. Data points at the same thickness partially represent different MBE runs; for example, the four 25-Å points represent two samples each from two different growths, the four 48-Å points, four different growths. For wide wells the data do not extrapolate to the 1.6-K bulk energy gap (0.81 eV) of GaSb, but to a value about 0.05 eV lower. A similar 50-meV discrepancy has been observed by Voisin *et al.*[4] in their absorption data. Those authors argue plausibly that this effect reflects a true gap narrowing caused by stress in the GaSb layer, due to the $\sim 0.6\%$ lattice mismatch between GaSb and AlSb.

The broken curve in Fig. 2 shows the calculated photon energy for quantum wells with a parabolic $\epsilon(k)$ relation. We assumed effective masses of 0.042 m_e and 0.144 m_e inside and outside the well (scaled linearly with energy gap), an adjusted GaSb energy gap of 0.76 eV, and a well depth of 1.5 eV (i.e., negligible valence-band offset). The discrepancy with the experimental data is far too large to be accounted for by incorrect well widths. We believe that it reflects the strong nonparabolicity of the Γ valley. The solid curve represents a fit to Bastard's model,[12] which includes this nonparabolicity to the first order. The details of the calculation will be published elsewhere.

We interpret the precipitous drop of the peak intensity of the Γ-transition peak in the 40–50-Å range (Fig. 1) as being due to the Γ valley moving above the X valleys. There does not appear to be a similar drop in intensity when the Γ valley is pushed above the L valleys around 90 Å. In fact, the PL intensity *increases* in going from $w \sim 120$ to $w \lesssim 100$ Å, with only a slight dip between 100 and 60 Å. The poor PL for wider wells was also observed by Naganuma *et al.*,[1] who attributed it to surface recombination in the wide GaSb layer at the top of their structures. Inasmuch as our top layers were AlSb layers, we suspect that the drop is due to misfit dislocations that form for $w \gtrsim 100$ Å, when the 0.6% lattice mismatch is no longer taken up fully by elastic strain. There remains the question as to why there is no significant drop in PL intensity with *decreasing* w around $w \sim 90$ Å, in contradiction to the data of Naganuma *et al.*[1] We speculate that the electrons in the L valleys have a very long lifetime (as in Ge), and that in our experiments with their much higher excitation intensity the recombination processes have saturated, leaving only the recombination path via the Γ valley to accommodate the high pump rate. This hypothesis implies the presence of a very high degree of band filling in the L and X valleys, which should manifest itself experimentally, but for which no search was made.

The most unexpected feature of all narrow-well PL spectra is the very broad and intense peak between the Γ luminescence peak and the bulk energy gap of GaSb. The peak shifts to lower energies as the well width is increased, but much less rapidly than the Γ peak itself, as is shown in the inset in Fig. 3. The intensity of this peak is relatively constant for well widths up to about 40 Å, above which it decreases, not only relative to the increasing Γ peak, but also absolutely. For well widths above 60 Å the secondary peak appears to be absent. The small but nonzero shift of this peak with well width, and its apparent disappearance when $\epsilon_\Gamma < \epsilon_X$ suggests that the peak is somehow related to electron accumulation in the X valleys. Note, however, that most of the intensity occurs in a very wide band at energies below ϵ_X, calling for an additional loss mechanism that involves an amount of energy that is both large and variable. One possibility is radiative recombination from the presumably highly populated X valleys to a very strongly phonon-broadened deep level in GaSb. Another possibility—which we favor—is a process in which two electrons from opposite X valleys recombine cooperatively, with one making a transition downward to the valence band, the other being lifted to the Γ valley, and the energy balance being emitted as a photon. Because the energy in the Γ valley can assume any one of a very wide range of values, a broad band of photon energies would result. Processes in which two electrons from opposing indirect valleys recombine under emission of a single photon have been observed in Ge and Si.[13] The process postulated here differs mainly in the sense that one of the electrons ends up in the central conduction-band valley rather than both in the valence band. Additional experiments needed to clarify this matter have been initiated.

We express our thanks to several individuals for extensive discussions, especially Bruce Hancock at UCSB and Dr. Ken Elliott at Rockwell. Professor M. H. Pilkuhn pointed out the relevance of Ref. 13 to our work. Thanks are also due to Don Zak for technical assistance. This work was supported by the Office of Naval Research.

[1] M. Naganuma, Y. Suzuki, and H. Okamoto, Inst. Phys. Conf. Ser. **63**, 125 (1982).
[2] C.-A. Chang, H. Takaoka, L. L. Chang, and L. Esaki, Appl. Phys. Lett. **40**, 983 (1982).
[3] E. E. Mendez, C.-A. Chang, H. Takaoka, L. L. Chang, and L. Esaki, J. Vac. Sci. Technol. B **1**, 152 (1983).
[4] P. Voisin, G. Bastard, M. Voos, E. E. Mendez, C.-A. Chang, L. L. Chang, and L. Esaki, J. Vac. Sci. Technol. B **1**, 409 (1983).
[5] Band structure data are taken from H. C. Casey and M. B. Panish, *Heterostructure Lasers* (Academic, San Francisco, 1978), Pt. B, Chap. 5.
[6] J. O. McCaldin, T. C. McGill, and C. A. Mead, Phys. Rev. Lett. **36**, 56 (1976).
[7] W. R. Frensley and H. Kroemer, Phys. Rev. B **16**, 2642 (1977).
[8] W. A. Harrison, J. Vac. Sci. Technol. **14**, 1016 (1977).
[9] The authors of Ref. 1 estimate the Γ/L crossover to occur below 80 Å, but they use an incorrect expression for the effective mass m^* that governs the shift of the bottom of the L valleys with well width. Their expression (2) should be replaced by $m^*_L(100) = (m_l + 2m_t)/3 \sim 0.51 m_0$.
[10] J. W. Matthews and A. E. Blakeslee, J. Vac. Sci. Technol. **14**, 989 (1977).
[11] Y. G. Chai and R. Chow, J. Appl. Phys. **53**, 1232 (1982).
[12] G. Bastard, Phys. Rev. B **10**, 5693 (1981).
[13] K. Betzler, W. Weller, and R. Conradt, Phys. Rev. B **6**, 1394 (1972).

On the (110) orientation as the preferred orientation for the molecular beam epitaxial growth of GaAs on Ge, GaP on Si, and similar zincblende-on-diamond systems

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Recent successful (110) growth of GaAs on Ge has prompted a reevaluation of the (110) orientation for the MBE growth of zincblende-on-diamond–type heterostructures. It is argued that the atomic geometry at a (110) interface should be particularly favorable for defect-free heteroepitaxy in such systems, for two reasons: (a) Recent work by Harrison *et al.* has shown that interfaces other than (110) interfaces in such systems must reconstruct. Such reconstruction will be incomplete, leaving behind hard-to-control interface charges. (b) The *free-surface* reconstruction of the diamond-structure (110) surface is such that it should favor subsequent growth of zincblende structures without antiphase domain boundaries.

PACS numbers: 61.50.Jr, 68.55. + b, 81.15.Ef, 82.65. − i

The (110) orientation has been the least commonly used low-index orientation for the epitaxial growth of semiconductors. In molecular beam epitaxy (MBE) it has hardly been used at all, the most important exception being the work by Bauer and McMenamin[1] on the growth of Ge on GaAs. We have recently studied the orientation dependence of the morphology of MBE growth of the inverse system, GaAs on Ge. Under the growth conditions employed,[2] (110) growth in this system had consistently the best morphology, approaching that of (100) homoepitaxial MBE growth of GaAs. Good (110) morphology has also been observed in the growth of GaP on Si.[3] The details of the growth procedures will be published separately; for the remainder of this letter they are irrelevant.

We believe that the significance of this result goes beyond the purely empirical aspect of the observation that under certain growth conditions the (110) morphology is excellent. The purpose of this letter is to point out that there are strong theoretical reasons, independent of morphology, to consider the (110) orientation as the preferred orientation for the MBE growth of heterojunctions (HJ's) that combine a zincblende-type semiconductor with the diamond-type semiconductors Ge or Si, and in which the interface itself is important for the device. These reasons would exist even if the empirical (110) morphology were inferior to that on other planes, so long as it is at least acceptable.

There are two separate reasons for the theoretical (110) preference: (a) Problems of electrical neutrality at the interface. They occur regardless of the growth sequence. (b) Problems of atomic disorder on the zincblende side. They occur only for the zincblende-on-diamond growth sequence.

The interface electrostatics problem was first recognized by Harrison *et al.* in an important paper,[4] hereafter referred to as HKWG. These authors investigated the electrostatics of idealized low-index interfaces in which the change from diamond to zincblende (or vice versa) was assumed to take place abruptly from one atomic plane to the next, without any reconstruction effects. They show that under these conditions there is associated with the interface a charge imbalance, which may be formally described as a net interface charage, with the two-dimensional density $e\sigma_i = ge/a^2$. Here a is the lattice constant of the two (lattice matched) semiconductors, and g is a geometrical factor the exact value of which depends on the interface orientation. Only for the (110) interface is $g = 0$. For the (100) interface, which has been most commonly used in MBE growth, $g = 1$. Similar magnitudes are obtained for other interfaces. Such a charge can support an electric field $E = e\sigma_i/\epsilon$. Numerically, for GaAs/Ge (100), $\sigma_i \cong 3\times 10^{14}$ cm^{-2}, $E \cong 4\times 10^7$ V/cm. As HKWG point out, the assumed idealized atomic arrangement at the interface would not be stable in the presence of such huge fields, and the interface would reconstruct. The authors give examples of the simplest reconstructed geometries that would lead to both zero interface charge and zero residual interface dipole.

Under realistic crystal growth conditions this reconstruction, although it will undoubtedly take place, is unlikely to proceed to completion. Inasmuch as it is the interface field that acts as driving force for the reconstruction, this driving force becomes weaker as the reconstruction proceeds, and hence the rate of reconstruction slows down. For any realistic growth process, finite residual interface fields must remain. It is exceptionally difficult to estimate exactly how large those residual fields are, but they will almost certainly be *at least* as large as the fields intentionally incorporated in *p-n* junction device structures. Otherwise it would not be possible to maintain these desired fields during device construction, in the presence of the same atomic diffusion processes that permit the reconstruction. Note that a field of about 4×10^5 V/cm would still be left after the reconstruction at a GaAs-Ge interface has proceeded 99% towards completion!

Such large residual fields will drastically affect the performance of any device structure in which the heterointerface is an essential part of the device rather than simply a substrate interface far away from the active region. In addi-

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tion to being undesirably large, the residual fields will vary strongly with small variations in technological parameters, making reproducibility hard to achieve. This is very likely one of the origins for the vast variations found in the extensively studied Ge-GaAs system. There is therefore a very strong incentive for working with an orientation for which the HKWG reconstruction problem does not exist, that is, the (110) orientation.

We now turn to the problems of atomic disorder on the zincblende side, if the zincblende-type semiconductor is grown on a diamond-type substrate. Consider the GaAs growth on Ge. The primitive crystallographic cell of Ge contains two atoms that are chemically identical and whose sites are energetically equivalent. The only difference between the two sites is the orientation of their four tetrahedral bonds in space. Based on this orientational difference, one might label all sites in the Ge substrate as either Ga(A) sites or Ge(B) sites, the choice between the two being a matter of convention. In GaAs the two kinds of sites are occupied by different atoms and hence are not equivalent. The problem in growing a defect-free GaAs-on-Ge HJ is to find a mechanism by which only As atoms are bonded to Ge(A) surface atoms and only Ga atoms to Ge(B) surface atoms, or vice versa. But in the absence of any energetic preference between the atoms, a Ga atom is equally likely to bond to either, as is an As atom, leading to antiphase disorder on the GaAs side of the HJ.

As first glance it would appear that the antiphase disorder problem is particularly severe on the (110) surface. The perfect (unreconstructed) Ge (110) surface consists of parallel rows of Ge(A) and Ge(B) atoms. If a GaAs crystal were *randomly* nucleated upon such a surface, a high density of antiphase domain boundaries on the GaAs side would result, as illustrated in Fig. 1(a). Arguments similar to those of HKWG show that the antiphase domain boundary would be highly charged, the sign depending on which way the two domains are oriented relative to each other. For the electrical properties of the HJ, such highly charged planes of defects would almost certainly be disastrous. In fact, one might argue that the electrostatic repulsion of oppositely polarized domains might delay the growing together of such domains, which would almost certainly lead to macroscopic deviations from a perfectly flat (110) morphology. Our observation of excellent (110) morphology contradicts this conclusion.

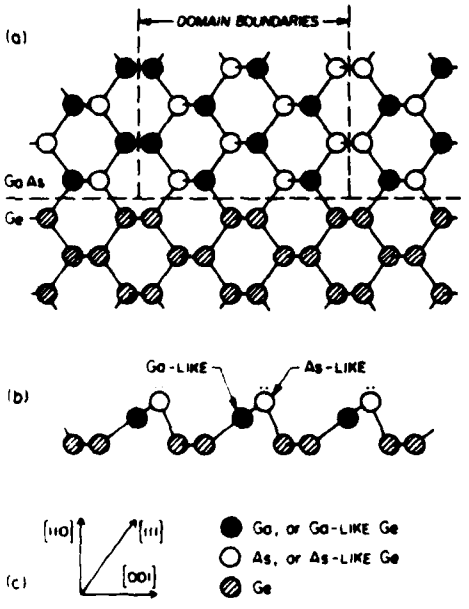

FIG 1 (a) Charged antiphase domain boundaries of alternating polarity caused by random Ga-As pairing on an unreconstructed Ge (110) substrate. (b) Creation of Ga- and As-like sites on Ge (110) substrate by reconstruction. (c) Identification of orientations and sites.

The important point is that *free* (110) surfaces are reconstructed under the conditions preceding growth inside an MBE system. Harrison[5] has postulated that on a Si (110) surface, one of the rows within each pair of parallel atomic rows should always be depressed below the unreconstructed surface, while the other row should be raised above it [Fig. 1(b)]. The same considerations should apply to Ge. This reconstruction is driven by a redistribution of the electrons, in such a way that the depressed row of atoms gives up one electron to the raised row. As a result, the electron configuration of the depressed row of Ge atoms mimics the electron distribution of Ga, while that of the raised row mimics As. In fact, this is exactly the geometry known to occur on GaAs (110), where it has been studied extensively in recent years.[6] Epitaxial of GaAs on a reconstructed Ge (110) surface should therefore closely resemble homoepitaxial growth on a GaAs (110) surface, with few if any site selection ambiguities. The only places on the surface where antiphase domain boundaries might be expected, are at domain boundaries in the initial surface reconstruction. Little appears to be known how large the surface reconstruction domains on either Si or Ge are, but it is clear that reconstruction domain boundaries are energetically unfavorable. It appears likely that large single-domain surface areas can be generated by suitable surface treatments, such as annealing before growth, or the application of thermal, electrical, or chemical gradients parallel to the surface. Quite likely, one of the most effective ways to creat the same domain orientation over a large surface area is to create phase-locking steps in the surface, by cutting the surface off the exact (110) plane by a small angle. We are currently investigating this matter experimentally.[2,3]

The situation on polar surfaces, such as (100) and (111), is quite different. If a polar surface were atomically flat without any steps, and in the presence of an expected strong chemical preference for As–Ge (or P–Si bonding over Ga–Ge (or Ga–Si) bonding, growth free of antiphase domain boundaries should also occur. However, all real crystal surfaces contain steps. On (100) surfaces, steps that are an odd number of atoms high must lead to antiphase domain boundaries. Such boundaries have indeed been reported by Morizane[7] to occur regularly in VPE growth. In contrast to the antiphase domain boundaries on an unreconstructed (110) surface, the atomic configuration of those occurring on (100) can be shown to be such that the boundaries would by electrically neutral, and hence of less consequence. This conclusion is supported by the observation that excellent photovoltaic cells[8] and Schottky barriers[9] can be prepared on GaAs layers grown on Ge (100) substrates. Probably the only effect

the (100) domain boundaries have is that they act as scattering planes, which reduce the mobility *parallel* to the heterointerface. Still, they are certainly not beneficial.

On a (111) surface, atomic steps an odd number of atomic layers high are energetically very unfavorable. Hence one would not expected to find antiphase domain boundaries, a prediction in agreement with the observations of Morizane.[7] However, heteroepitaxial growth of GaAs on Ge on the (111) surface usually exhibits a poor morphology for other reasons, such as stacking faults.[10]

Evidently, the favorable properties of the (110) orientation with respect to disorder on the zincblende side depend strongly on whether or not the postulated reconstruction with its universal bond rotation actually takes place. This bond rotation would not change the group symmetry of the surface point lattice, and hence its only major effect on any LEED pattern would be that those reflections that are forbidden for an unreconstructed Ge or Si surface would now have a finite intensity, resembling a GaAs LEED pattern. The observed LEED patterns[11,12] reveal more-complex surface geometries, which contain symmetry-breaking atomic rearrangements. They are probably superimposed upon the basic bond rotation, but there do not appear to exist any quantitative data about the energy dependence of Ge and Si (110) reflection intensities to decide this question, as was done for GaAs (110).[6] If the universal bond rotation persists, the additional reconstruction should not affect the nucleation.

It would clearly be desirable to have more direct data on these matters rather than only the indirect evidence of our observations[2,3] on morphology. To be truly relevant to MBE growth, such data should not be on room-temperature clean surfaces, but on hot surfaces exposed to As or P molecular beams: reconstruction patterns are known to be sensitive to very small amounts of impurities,[11] and As or P beams are almost always present before actual growth in MBE. In fact, the sensitivity of the reconstruction of GaAs (100) surfaces to be As:Ga flux ratio is a well-known integral part of MBE technology. Elementary chemical arguments suggest that on a Ge (110) surface the presence of As will strongly favor a reconstruction that generates Ga-like sites, to which the As can then bond, which leads directly back to Harrison's argument.[5] An analogous argument applies to P on Si (110).

The likely influence of the chemical environment on the details of reconstruction means that our conclusions are not necessarily applicable to technologies other than MBE, in which a different chemical environment may lead to different reconstruction and hence nucleation.

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[1]R.S. Bauer and J.C. McMenamin, J. Vac. Sci. Technol. **15**, 1444 (1978).
[2]K.J. Polasko and H. Kroemer (unpublished). The most essential growth parameters were as follows: substrate temperature 350–500 °C, growth rate $\cong 0.1\ \mu$m/h, As_4:Ga flux ratio > 10. We do not know to what extent these conditions are important for good (110) morphology.
[3]S. Wright and H. Kroemer (unpublished).
[4]W.A. Harrison, E.A. Kraut, J.R. Waldrop, and R.W. Grant, Phys. Rev. B **18**, 4402 (1978).
[5]W.A. Harrison, Surf. Sci. **55**, 1 (1976).
[6]For a recent review, see C.B. Duke, CRC Crit. Rev. Solid State Mater. Sci. **8**, 69 (1978).
[7]K. Morizane, J. Cryst. Growth **38**, 249 (1977).
[8]J.C.C. Fan, C.O. Bozler, and B.J. Palm, Appl. Phys. Lett. **35**, 875 (1979).
[9]D.L. Miller (private communication).
[10]T. Gabor, J. Electrochem. Soc. **111**, 817, 821, 825 (1964).
[11]F. Jona, IBM J. Res. Dev. **9**, 375 (1965).
[12]B.Z. Olshanetsky, S.M. Repinsky, and A.A. Shklyaev, Surf. Sci. **64**, 224 (1977); B.Z. Olshanetsky and A.A. Shklyaev, *ibid.* **67**, 581 (1977).

Simple rate equation model for hypothetical doubly stimulated emission of both photons and phonons in quantum-well lasers

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The dissipation processes by which electrons and holes lose energy after being trapped in quantum wells might, in a sufficiently heavily pumped quantum well laser, lead to the buildup of such a high phonon population that phonon-assisted laser action by doubly stimulated emission of photons and phonons acquires a higher gain than unassisted laser action. The resulting mode switching exhibits a pronounced hysteresis with pump rate, which should be a characteristic identifying feature of phonon-assisted laser action.

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In a recent series of papers,[1-3] Holonyak and Dapkus, together with varying co-workers, presented data on GaAs-(Al, Ga) As quantum-well lasers, which they interpret as evidence for phonon-assisted laser action, with the phonon emission itself being stimulated. We refer here to this combination as doubly stimulated emission (DSE). The data indicate great variability from sample to sample and, for a given sample, with variations in excitation conditions. Others[4] have failed to observe the same spectral features, and have interpreted differently those features that they do observe. Hence, it would be premature to assume that the idea of DSE has been universally accepted.

Phonon-assisted processes are higher-order processes, which tend to have much lower probabilities than unassisted processes, unless the latter are somehow forbidden. In laser action in a direct-gap semiconductor, in which unassisted laser action is allowed, phonon-assisted processes should have much lower gain than unassisted laser action, except in the presence of a very high (nonthermal) phonon polulation. All available evidence is that in *bulk* GaAs the laser action is not phonon-assisted. Once stimulated emission of phonons sets in, a high phonon population could be maintained by this process, but the initial phonons must originate some other way. The Illinois/ Rockwell work suggests that phonons are generated by electrons losing energy in falling from the top of the deep quantum wells to the lasing energy levels further down. We call such phonons here *percolation phonons*.

In the present letter we attack this problem by asking the following questions: Suppose DSE, triggered by percolation phonons, *does* indeed exist, what exactly *should* be its key properties? Does the excercise lead to testable predictions that one might use to distinguish DSE from more mundane effects? We believe that such an inquiry is valid in its own right, regardless of the resolution of any questions concerning the Illinois/Rockwell data, and it may aid in this resolution.

We discuss here the simplest possible model of DSE, containing only the essential ingredients of the physics, ignoring everything one might view as nuisance complica-

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tions. We assume only one unassisted and one assisted photon mode, and one phonon mode. We assume that the rates of generation for unassisted photons, for assisted photons, and for phonons are the following:

$$g_0 = (I/\tau_U)(n_0 + 1), \tag{1}$$

$$g_- = (I/\tau_A)(n_- + 1)(p + 1), \tag{2}$$

$$g_p = mg_0 + (m + 1)g_-. \tag{3}$$

The various symbol have the following meaning: I is the population inversion (number of electron-hole pairs) in the laser cavity. τ_U and τ_A are characteristic time constants for unassisted and assisted processes. Presumably $\tau_A \gg \tau_U$. n_0, n_-, and p are the two photon occupation numbers and the phonon occupation number. The factor m is the number of percolation phonons generated *into the recombination-assisting phonon mode* per recombining electron-hole pair. Percolation phonons that arise from electron-hole pair recombination processes other than by stimulated emission, although beneficial, are neglected for simplicity, and to obtain rate equations that can be solved in closed form.

We assume the following rate equations

$$dn_0/dt = g_0 - n_0/\tau_0, \tag{4}$$

$$dn_-/dt = g_- - n_-/\tau_-, \tag{5}$$

$$dp/dt = g_p - (p - p_0)/\tau_p, \tag{6}$$

$$dI/dt = R - (g_0 + g_-) - I/\tau_I. \tag{7}$$

Here, τ_0 and τ_- are the cavity lifetimes for the two photon modes. τ_p is the phonon lifetime. p_0 is the thermal equilibrium phonon occupation number. R is the laser pump rate. τ_I is the lifetime of the population inversion due to all processes other than stimulated emission.

In this letter, we consider only steady-state solutions, $d/dt = 0$. In this case, one obtains from (1) and (4), and from (2) and (5)

$$g_0 = (1/\tau_0)\, I\sigma_0/(1 - I\sigma_0), \tag{8a}$$

$$g_- = (1/\tau_-)\, I\sigma_-/(1 - I\sigma_-), \tag{8b}$$

where $\sigma_0 = \tau_0/\tau_U$ and $\sigma_- = (p + 1)\tau_-/\tau_A$. If (8a) and (8b) are inserted into (3), and the result into (6) for $d/dt = 0$, one obtains

$$\frac{p - p_0}{\tau_p} = \frac{m}{\tau_0}\frac{I\sigma_0}{1 - I\sigma_0} + \frac{m + 1}{\tau_-}\frac{I\sigma_-}{1 - I\sigma_-}. \tag{9}$$

This is a quadratic equation in I, which yields I as a function of p. Of the two roots of (9) the lower root is the physically relevant one; the higher root corresponds to an unphysical solution in which both g_0 and g_- remain large as $p \to p_0$, with opposite signs. Insertion of $I(p)$ into (8a) and (8b) yields the two (internal) photon emission rates, and further insertion of g_0, g_-, and I into (7) yields the pump rate.

We have performed such calculations for a wide range of parameters. Figures 1 and 2 show a typical result, calculated for the following parameter values:

$$\tau_0 = \tau_- = 10^{-11}\ \text{s},\ \tau_I = 10^{-9}\ \text{s},\ \tau_p = 10^{-12}\ \text{s},$$

$$\tau_I/\tau_U = 10^{-2},\ \tau_A/\tau_U = 10^2,\ m = 0.1,\ p_0 = 1.$$

Their choice will be discussed later.

Figure 1 shows the electron population inversion I versus the phonon occupancy. After an initial quick rise with increasing p, the population inversion stays essentially unchanged over a range of p two decades wide. This reflects the familiar pinning of the population inversion with increasing pump rate in simple laser theories. Throughout this range the laser action is dominated by the unassisted transition. If the phonon population is increased beyond that critical value $p_c = \tau_A\tau_0/\tau_U\tau_-$ above which the assisted mode has a higher gain than the unassisted mode, the inversion level drops roughly inversely proportional to the phonon occupation number, and the laser action changes from unassisted to assisted.

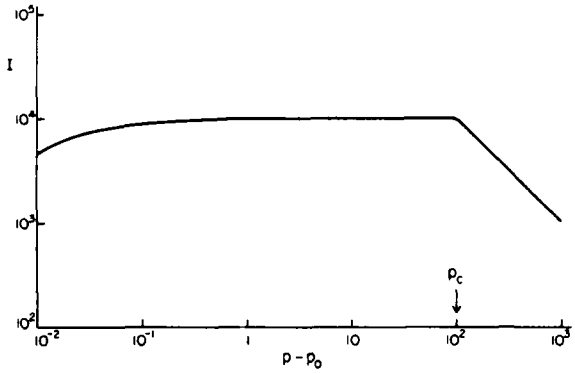

FIG. 1. Steady-state population inversion I associated with a given steady-state phonon population, for the model parameters quoted in the text. The wide flat range reflects inversion level pinning prior to the onset of phonon-assisted laser action.

The two (internal) photon emission rates, plotted as functions of the pump rate, exhibit a remarkable behavior, shown in Figs. 2(a) and 2(b), where we plot the ratios g_0/R and g_-/R *against* R. *Over a certain range of pump rates,* $R_l < R < R_u$, both curves are triple valued. Experimentally, the pump rate is the controlled variable, not the phonon occupation number. At the two ends of the triple-valued range the laser changes its behavior discontinuously with changing pump rate, as indicated by the arrows in Figs. 2(a) and 2(b). As the rate R_u is exceeded, the laser action switches abruptly to nearly pure assisted laser action. If the pump rate is subsequently lowered, the assisted laser action remains

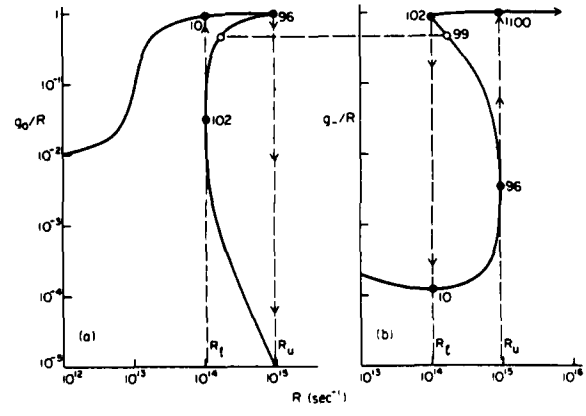

FIG. 2. Unassisted (left) and assisted (right) photon emission rates, divided by the pump rate, as functions of pump rate, for the model parameters given in the text. Both processes exhibit hysteresis, with abrupt mode switching at $R = R_l$ and $R = R_u$, indicated by vertical arrows. The numbers plotted at selected points along the curves are phonon occupation numbers. The two curves cross over for $p = 99$.

dominant until the lower rate R_l is reached, at which point the laser action switches back to nearly pure unassisted action.

The underlying physics is simple: As the pump rate is raised, few phonons are initially present, and the laser action proceeds mainly unassisted until p approaches p_c. As $p \to p_c$, a small increase in R will lead to a small increase not only in g_0 but also in g_-. The latter will generate additional phonons by stimulated emission, which will in turn increase the assisted emission rate at the expense of the unassisted rate. This creates additional phonons, etc. Above a certain pump rate R_u this feedback process becomes unstable and phonon runaway takes place, until almost the entire pump rate is consumed by assisted emission events. If the pump rate is subsequently reduced, the phonon population decreases again, but does not switch back until once more $p \approx p_c$, at which point the pump rate has dropped to the lower value $R_l < R_u$.

We believe this predicted switching behavior with hysteresis to be a characteristic feature of DSE. None of the experimental reports mention such a hysteresis. This may simply reflect the absence of any search for this behavior. If such a hysteresis can not be achieved, this should be considered a strong argument against DSE. If it were found, it should be considered an equally strong argument for DSE.

The adjustable parameters used in Figs. 1 and 2 were chosen so as to bring out the characteristic features of DSE, as opposed to unassisted laser action, and as they might appear in experiments designed to enhance these features. No attempt was made to match parameters in the published experiments,[2] which were not designed to bring out these features. Furthermore, several parameters were deliberately chosen on the conservative side, not strongly favoring DSE. This was done to indicate that, once some percolation phonons are present, assumptions otherwise favoring DSE are in fact not necessary for DSE to manifest itself. The values of τ_0, τ_l, and τ_p are reasonably realistic, the latter two on the conservative side. The value of τ_- should be somewhat larger than τ_0; setting $\tau_- = \tau_0$ is again conservative. The ratio τ_l/τ_U is the fraction of the recombination events that go into the laser mode ω_0 *before* the onset of laser action. A high value of τ_l/τ_U was chosen to compensate for the omission of percolation phonons generated by recombination processes other than those in g_0 and g_-. The ratio τ_A/τ_U was chosen to yield $p_c = 10^2$. This is significantly higher than the values claimed by the Illinois/Rockwell group[2] ($p_c < 10$), to be on the conservative side of what we consider an optimistic estimate. There do not appear to exist any reliable estimates of what the ratio τ_A/τ_U should be on theoretical grounds. The magnitude of p_0 is realistic but irrelevant: Only the below-threshold behavior depends non-negligibly on p_0; we could just as well have set $p_0 = 0$.

The most important assumption is that about the magnitude of m. The total number of percolation phonons per electron is certainly large compared to unity; but m represents only those phonons that go into the radiation-assisting mode. If the percolation phonons were emitted randomly into all availabe phonon modes, this would correspond to a very much smaller value of m than 0.1, and the bootstrapping process via percolation phonons would not work. However, it must be expected that phonon generation by scattering, like other boson emission processes, will favor emission into those modes that are already most heavily populated. Hence the assumption of a non-negligible m value is probably realistic and, *if so*, our value $m = 0.1$ is probably conservative. Clearly, $m \gtrsim 1$ is not necessary to obtain DSE. Assuming parameters more favorable to DSE than we have done ($\tau_0 < \tau_-$, smaller p_c, larger m) reduces R_u, narrows the hysteresis, and may lead to a switch over to the DSE mode substantially before the unassisted efficiency g_0/R has saturated. If, contrary to expectations, the conditions in GaAs should be *very* favorable to DSE, the hysteresis could be so narrow as to be hard to observe, but in this event it is always possible to create experimental conditions less favorable to DSE, thereby widening the hysteresis and demonstrating the DSE nature of the process.

In summary, the simple rate equation model predicts that phonon-assisted laser action by DSE of both photons and phonons should indeed take place, provided the key assumption is satisfied, that the percolation phonons are generated preferentially into those phonon modes that are already most heavily populated, which subsequently assist the photon emission. The theory retains essentially the same form if several phonon (and photon) modes are assumed to contribute equally, with p the phonon ouccupancy per mode and m the number of percolation phonons per mode. Our example with $m \ll 1$ already makes allowance for this possibility.

We are currently studying this model (and its justification) in more detail. The results will be reported in due course.

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[1] For a review through late 1979 see N. Holonyak, Jr., R. M. Kolbas, R. D. Dupuis, and P. D. Dapkus, IEEE J. Quantum Electron. **QE-16**, 170 (1980).
[2] J. J. Coleman, P. D. Dapkus, B. A. Vojak, W. D. Laidig, N. Holonyak, Jr. and K. Hess, Appl. Phys. Lett. **37**, 15 (1980).
[3] N. Holonyak, Jr., B. A. Vojak, W. D. Laidig, K. Hess, J. J. Coleman, and P. D. Dapkus, Appl. Phys. Lett. **37**, 136 (1980).
[4] W. T. Tsang, C. Weissbuch, R. C. Miller, and R. Dingle, Appl. Phys. Lett. **35**, 673 (1979).

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