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LPE $In_{1-x}Ga_xP_{1-z}As_z$ ($x \sim 0.12$, $z \sim 0.26$) DH laser with multiple thin-layer (<500 Å) active region[a)]

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A liquid-phase-epitaxial (LPE) double-heterojunction (DH) laser structure with an ~1-μm "active region" consisting of ≳20 $In_{1-x}Ga_xP_{1-z}As_z$ and InP lattice-matched thin layers is described. The thin-layer dimensions are small enough (<500 Å) to make quantum size effects relevant.

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Utilizing molecular-beam-epitaxy (MBE) for the growth of successive thin crystal layers,[1] Bell Laboratories and IBM workers have reported a number of multilayered III-V semiconductor structures in which the individual layers are thin enough to lead to quantum size effects (QSE). (For a review and list of references see Refs. 2 and 3.) Depending upon the III-V materials employed, these effects are observable at layer thicknesses ≲500 Å.[4] A question of considerable interest is whether *multilayered* structures, with layer thicknesses ≲500 Å, can be grown by other methods, for example, by liquid-phase epitaxy (LPE). For this to be possible several conditions must be met: (1) the LPE growth should be practical at low enough temperatures to minimize cross diffusion of impurities or the crystal atoms themselves; (2) the crystal growth should be slow enough to allow control of the layer thicknesses; and (3) the crystal growth, involving at least two LPE melts (two different lattice-matched III-V materials), should be capable of being interrupted and restarted without contamination or layer damage and without melt carry-over or incomplete wipe-off being a serious problem.

It is likely that a number of III-V systems will satisfy these conditions. For example, in earlier work[5] *single* LPE layers of GaAs as thin as ~400 Å and single $Ga_{1-x}Al_xAs$ layers as thin as ~800 Å have been grown in DH lasers. In the present work we show that a *multilayer* structure consisting of alternate thin layers of InP and lattice-matched $In_{1-x}Ga_xP_{1-z}As_z$ can be grown via LPE with layer thicknesses <500 Å. A "double-heterojunction" (DH) laser diode is demonstrated in which ≳20 thin layers (<500 Å) of InP and $In_{1-x}Ga_xP_{1-z}As_z$ ($x \sim 0.12$, $z \sim 0.26$) are incorporated into the "active region" (~1 μm) of the structure.

As is well known,[6] $In_{1-x}Ga_xP_{1-z}As_z$ of energy gap ≲1.35 eV can readily be grown via LPE at low temperature (600–650 °C) lattice matched to InP. In the present work the cylindrical graphite boat[7] and the constant-temperature LPE crystal growth procedure used in earlier work to grow visible-spectrum $In_{1-x}Ga_xP_{1-z}As_z$ DH lasers[8] is used to grow (640 °C) lattice-matched alternate thin layers of InP and $In_{1-x}Ga_xP_{1-z}As_z$. The quaternary crystal growth rate can be adjusted so that good control of layer thickness can be achieved, while at the same time the quaternary composition, and lattice matching, remain constant even when the LPE process is interrupted and repeated.[9] Typically the quaternary melt is arranged to be saturated at 650 °C and consists of 4.5 g In, 0.0256 g InP, 0.1937 g InAs, and 0.0160 g GaAs. This melt composition (at a growth temperature of 640 °C) results in LPE $In_{1-x}Ga_xP_{1-z}As_z$ ($z \sim 0.12$, $z \sim 0.26$) of energy gap ~200 meV less than InP. The details of the crystal growth procedure and the rather slight problems of achieving lattice match to InP are described elsewhere.[9]

Because of the simple design of the cylindrical graphite slider boat,[7] it is an easy matter to rotate an InP

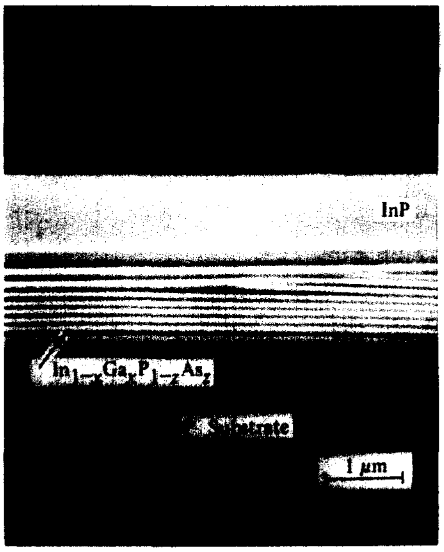

FIG. 1. Scanning electron photomicrograph of a layered LPE $In_{1-x}Ga_xP_{1-z}As_z$ ($x \sim 0.12$, $z \sim 0.26$) DH structure. Eleven quaternary layers, appearing as dark bands (arrow), and ten *n*-type InP layers form an ~1-μm DH active layer. Several of the final quaternary and InP layers are obscured by Zn diffusion from the *p*-type InP capping layer. The deterioration of well-defined layers, beginning after layer 12, is apparently due to melt carry-over (incomplete wipe-off). (Slight curvature of the cross section due to sample alignment and focusing difficulties.)

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substrate crystal first into contact with a pure In melt in order to dissolve several microns of the substrate (to remove thermal damage and oxides[10]) and next into contact with an InP melt to grow a planar surface on the substrate. Then the substrate is rotated (manually) back and forth, 20 or more times, into contact with the quaternary and then with the InP melt (in an ~1-sec cycle) to grow the multiple thin layers of main interest. Finally the substrate is rotated into contact with a Zn-doped InP melt to grow a p-type capping layer.

The multilayer heterostructure resulting from the above growth procedure is shown in the SEM photomicrograph of Fig. 1. Due to the higher etching rate of $In_{1-x}Ga_xP_{1-z}As_z$ than InP,[9] the quaternary layers appear as dark bands. This is evident also from the appearance of the top thick InP layer. Because of the high magnification and sample alignment problems, only the LPE layers are in focus (not the substrate). The slight curvature of the LPE layers is due to sample-alignment problems in the SEM. The first 12 layers (starting with an InP layer, not labeled) are highly uniform and evenly spaced. Then beginning on the right and running toward the center of Fig. 1 two sets of layers merge and at the left appear thickened, i.e., on the left side of Fig. 1 two quaternary layers are lost. This flaw in the growth probably occurs because of incomplete melt wipe-off between the growth of one layer and another. Note, however, that the LPE crystal specimen used for Fig. 1 was taken from the edge of the growth region, not from the center where the surface morphology appears as good as for high-quality standard DH wafers.[11] At the top of the multilayer region several layers appear smeared, but this is actually the effect of Zn diffusion from the top capping layer and the more rapid etch rate of p-type material. In contrast to mismatched structures,[9] no dislocation etch pits can be observed in the structure of Fig. 1; this is taken as evidence that the

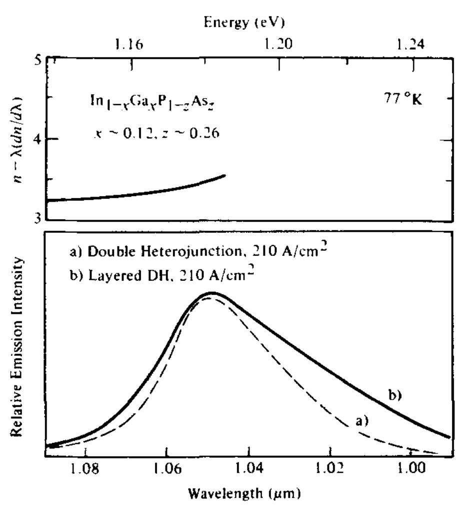

FIG. 2. Comparison of spontaneous emission (77 °K) of a standard $In_{1-x}Ga_xP_{1-z}As_z$ ($x \sim 0.12$, $z \sim 0.26$) DH diode (a) and a layered DH diode (b) (same current level). The peak emission occurs at nearly the same wavelength for each diode but the layered DH shows considerably more relative emission at high energy apparently due to quantum size effects (see Ref. 4). The effective index of refraction ($n - \lambda dn/d\lambda$) for the layered DH diode was determined from expanded spectra exhibiting uniform modes extending over a large wavelength range (~ 840 Å) and is significantly smaller than for standard quaternary DH lasers.

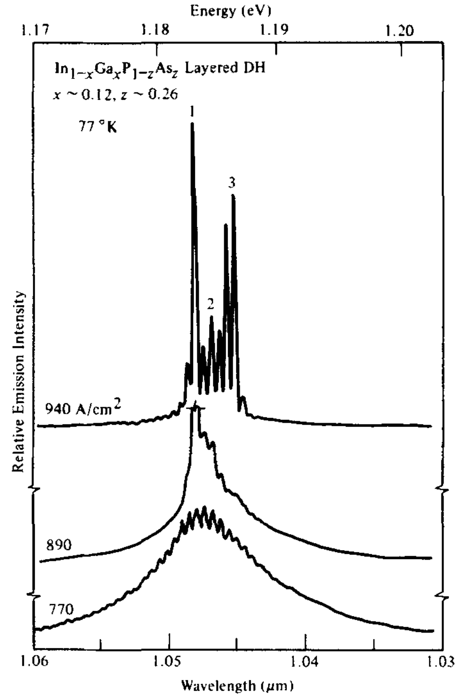

FIG. 3. Stimulated emission spectra (77 °K) of a layered $In_{1-x}Ga_xP_{1-z}As_z$ ($x \sim 0.12$, $z \sim 0.26$) DH structure. Below threshold (770 A/cm²) the diode exhibits uniform modes (amplitude and spacing). At 890 A/cm² laser operation occurs predominantly on one mode (1, cropped). At higher excitation (~ 940 A/cm²) three groups of laser modes are present (typical case) with a spacing $\Delta E_{12} = 1.3$ meV and $\Delta E_{13} = 3.3$ meV, agreeing with the layer dimensions and the possibility of quantum size effects [i.e., $\Delta E_{13} \sim \Delta E_{12}(8/3)$].

lattice match is preserved across all the LPE layers.

Although the LPE multilayer structure of Fig. 1 is not ideal, in large regions it is highly regular and has been fabricated into laser diodes. Diode spontaneous emission behavior is shown in Fig. 2 (curve b) and is compared with standard quaternary DH laser diodes (curve a) of the same ($x \sim 0.12$, $z \sim 0.26$) composition. The peak emission wavelengths agree remarkably well, but the emission (curve b) extends noticeably to higher energy. Because this behavior is typical of *all* diodes of this work, we assume, from the thinness of the quaternary layers (< 500 Å), that this is a manifestation of QSE and the change in density of states that occurs above the band edge.[4] The spectral broadening that is observed is known to be unrelated to melt depletion. In other work[9] on the quaternary ($x \sim 0.12$, $z \sim 0.26$) the melt depletion *per micron* of LPE growth has been measured to be 0.002% In, 0.08% Ga, 0.36% P, and 0.02% As. Clearly melt depletion for 12 or more quaternary layers as in Fig. 1 (12×0.05 μm) is insignificant. Note also that the broadening that occurs on the higher-energy side of the spectrum of Fig. 2 is not associated with any of the InP layers; *no* InP emission ($\lambda \sim 0.91$ μm, 77 °K) is observed.

That QSE might play a role in the behavior of these diodes agrees with the laser data shown in Fig. 3 (as well as, of course, the dimensions of the layers in Fig. 1). At an excitation level of 770 A/cm² *uniform* modes are observed across the peak of the recombination spectrum; above laser threshold (890 A/cm^2) a large laser mode is evident (1, cropped), and at still higher current (940 A/cm^2) a group of modes labeled 2 and a group labeled 3 appear. There is some suggestion, at 890 A/cm^2, that these modes exist. At higher currents than 940 A/cm^2 the group of modes 2 appear noticeably different from those labeled 1 or 3. This behavior is typical of these diodes; in contrast, standard $In_{1-x}Ga_xP_{1-z}As_z$ DH laser diodes (Fig. 2) exhibit a uniform spectrum of laser modes.[11,12] We note further that the modes labeled 1 are centered ~1.3 meV from the 2 modes and ~3.3 meV from the 3 group of modes, which as an estimate agrees with $(1.3)(\frac{8}{3})$. This behavior corresponds fairly well with what would be expected[4] based on the relatively large layer dimensions in Fig. 1 and the fact that the lower-lying levels of a confined particle (electron in a quaternary layer) tend to approach one another as the layer thickness increases to ~500 Å (see Fig. 3 of Ref. 4).

As for previous (conventional) $In_{1-x}Ga_xP_{1-z}As_z$ DH lasers,[12] the diodes of interest here exhibit spontaneous emission cavity modes (at low and high levels) extending over a large range (~840 Å). From the mode spacing ($\Delta\lambda$) the effective index of refraction ($n - \lambda\, dn/d\lambda$) can be determined and is shown in Fig. 2. Of particular interest is the fact that the effective index is significantly smaller (3.2 versus 3.5) at lower energies and also in the region of stimulated emission (3.5 versus 3.8) than in previous $In_{1-x}Ga_xP_{1-z}As_z$ DH lasers.[11,12] In addition, the effective index does not change much with excitation level,[12] i.e., remains near 3.5 in the peak emission region where stimulated emission occurs. The low index that is observed is a manifestation of the layered nature of the "active region" waveguide (and not QSE).

Of main interest in this work is the fact that a multilayered structure, with thin individual layers (< 500 Å, Fig. 1), can be grown by LPE. Because no special effort beyond previous work (boat design, mechanized slider, or improved melt wipe-off) has been made to grow the structure of Fig. 1, considerable improvement should be possible, perhaps leading to layer thicknesses ~50 Å.

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On the determination of charge centroids in insulators by photoinjection or photodepopulation

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Under certain conditions the centroid of a trapped charge distribution in an MOS insulator can be determined from charge and flatband shift measurements during photoinjection or photodepopulation. This technique was applied earlier by Harari and Royce, who made an erroneous assumption in deriving their equation. The correct equations are derived in the present letter, and the trap structure of pyrolytic Al_2O_3 films is reinterpreted.

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When charge is injected into or released from an MOS insulator, it is possible under certain conditions to determine the centroid of the charge distribution from measurements of external current and *C-V* curve flatband shifts. In the case of photodepopulation of traps there must be negligible retrapping of carriers. With trap filling by photoinjection (or other electrode injection) conduction currents must be negligible; i.e.,