Gas-source molecular beam epitaxial growth, characterization, and light-emitting diode application of $In_xGa_{1-x}P$ on GaP(100)

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(Received 24 September 1992; accepted for publication 15 February 1993)

Highly lattice-mismatched $In_xGa_{1-x}P$ ($x \leqslant 0.38$) layers were grown on GaP substrates by gas-source molecular beam epitaxy. A relatively thin, compositionally linear-graded buffer layer was used to reduce the number of threading dislocations. Studies by double-crystal x-ray diffraction and transmission electron microscopy show this buffer layer to be 97% strain-relaxed along both ⟨110⟩ directions with dislocations well confined within the graded buffer and the substrate. Threading dislocation densities in the top layers were less than 1×10^7 cm^{-2}. Room-temperature photoluminescence, ranging from 560 to 600 nm, is achieved. Heterojunction *p-i-n* diodes emitting at 560 nm at 300 K exhibit good rectifying and reverse breakdown characteristics.

Visible light-emitting diodes (LEDs) and laser diodes are useful for outdoor displays, signaling, and laser printers. Red $GaAs_xP_{1-x}$ LEDs and green GaP LEDs have been mass-produced for years by liquid- or vapor-phase epitaxy. In these indirect-band-gap materials impurity-induced transitions are responsible for the light generation. However, a typical external quantum efficiency for a $GaAs_xP_{1-x}$ LED at 590–630 nm, for example, is less than 1%. LEDs made with a direct-band-gap material show much higher efficiencies. Lattice-matched InGaAlP LEDs grown on GaAs, with the help of a thick GaP window layer, achieved a 6% external quantum efficiency at 590 nm.[1] At 560 nm the same structure with a higher aluminum content exhibits a lower efficiency ($\approx$0.2%), but still better than a conventional green GaP LED ($\approx$0.08%).[1]

An alternative approach to indirect-gap GaAsP and direct-gap InGaAlP on GaAs for achieving room-temperature, short-wavelength visible light emission is to grow a lattice-mismatched epilayer of direct-gap $In_xGa_{1-x}P$. When $x>0.27$, this material has the highest direct-band-gap of any arsenide or phosphide, except $In_xAl_{1-x}P$. It grows tensilely strained on GaAs ($x<0.49$) or compressively strained on GaP. In the composition range $0.27<x<0.49$, similar band gaps to that of InGaAlP lattice-matched to GaAs can be achieved without using aluminum, an advantage since aluminum is very sensitive to oxygen contamination. Recently, Masselink and Zachau reported the growth of $In_{0.35}Ga_{0.65}P$ on GaAs and obtained a room-temperature peak emission at 590 nm.[2] Stinson *et al.* have grown thick (10 μm) $In_xGa_{1-x}P$ layers on a graded buffer layer on GaP by organometallic vapor-phase epitaxy and reported an LED external quantum efficiency of 0.9% at 590 nm.[3] GaP substrates have the advantage that they are transparent to the emitted light, hence substrate absorption is greatly reduced. In this letter, we report the growth and characterization of $In_xGa_{1-x}P$ layers grown on a relatively thin (compared to Ref. 3), linearly graded buffer layer on GaP (100) by gas-source molecular beam epitaxy (GSMBE). The device characteristics of double-heterojunction $In_xGa_{1-x}P$ green (560 nm) LEDs are also described.

Matthews *et al.*[4] predicted that mismatched epilayers could have lower dislocation densities than the substrate because the misfit strain energy would cause existing threading dislocations to glide out of the epilayer. However, at large lattice mismatch this model breaks down since substrate dislocation densities are insufficient to relax the strain entirely. The nucleation of new dislocations is required, and this process is less well understood or controlled. Compositionally step-graded[5] or linearly-graded buffer layers[6–9] for strain relaxation and dislocation filtering in large mismatched systems have recently been reexamined. The results for both III-V and group IV semiconductor systems have been encouraging. Fitzgerald *et al.*[6] demonstrated low threading-dislocation densities in Si_xGe_{1-x}/Si using a linearly graded buffer layer. Using a similar technique, Lord *et al.*[7] reported 1.3 μm exciton resonance in an $In_{0.5}Ga_{0.5}As$ multiple quantum well structure grown on GaAs. Fischer–Colbrie *et al.*[8] reported obtaining high-quality $In_{0.8}Ga_{0.2}As$ on InP, and Le Goues *et al.*[9] reported low threading dislocation densities in both the Si_xGe_{1-x}/Si and $In_xGa_{1-x}As$/GaAs systems. Appropriately graded structures produce a sufficient amount of misfit dislocations to relax the film at a nucleation rate slow enough to apparently allow the glide of threading dislocations unimpeded to the edges of the sample. In this work we apply this growth technique to the $In_xGa_{1-x}P$/GaP system and obtain $In_xGa_{1-x}P$ buffer layers with threading dislocation densities sufficiently low as to serve as a substrate for further growth.

The growth was performed in an Intevac Modular GEN-II MBE modified to handle arsine and phosphine.

Pure phosphine was introduced into the growth chamber through a cracker producing P_2 and H_2. Solid gallium and indium were used for the group-III sources. More details about the GSMBE system have been described elsewhere.[10] The n-type GaP (100) substrate was cleaned with a HCl:HNO_3: H_2O (4:4:5) solution and mounted with indium onto a 3-in. Si wafer before it was loaded into the growth chamber. Oxide desorption occurred at about 660 °C. A thin GaP layer was grown first at 650 °C followed by the graded $In_xGa_{1-x}P$ buffer layer. For the buffer layer the indium cell temperature was changed at a rate such that the indium composition increased by 1% for every 40 nm of layer grown, approximately 2% lattice mismatch per micron. Because of the lower melting point of InP, compared to GaP, the optimal growth temperature is approximately in proportion to the In composition. Therefore, the substrate temperature was gradually decreased from 650 °C to the final temperature (490 to 550 °C) for the growth at the composition $x \approx 0.3$. The growth of the buffer layer was interrupted four times while the substrate was annealed for 5 min at 60 °C higher than the growth temperature. We found that this thermal cycling improved the surface morphology. After the required indium composition was reached, a constant-composition layer for x-ray diffraction measurements or diode fabrication was grown on top.

The surface of each sample was examined under a Nomarski optical interference microscope. Clearly defined surface cross-hatch patterns along both in-plane ⟨011⟩ directions were observed on these films, similar to previous work on lattice-mismatched epitaxial growth.[9] This cross-hatched surface could be related to misfit dislocation multiplication sources whereby repeated glide occurs on closely spaced ⟨111⟩ planes.[11] We found the cross-hatched surface morphology to be associated with a low threading dislocation density and an intense photoluminescence (PL) emission.[9] Another sample of $In_{0.32}Ga_{0.68}P$ grown with a four-step graded buffer layer (8% indium per step) has a rough textured surface and no PL response at room temperature. A clearly defined cross-hatched surface pattern then served as a first qualitative evaluation of the epilayers before further characterization.

Figure 1 shows a cross-section transmission electron micrograph (XTEM) of an $In_{0.32}Ga_{0.68}P$ epilayer grown on a linearly graded buffer on GaP(100). The TEM was carried out at an accelerating beam voltage of 300 kV. Dislocations are mostly confined to the graded buffer layer. Dislocation loop pile-ups in the substrate are also observed.[12] The top layer with a constant composition is clear and free of dislocations in XTEM. The threading dislocation density estimated from plan-view TEM is less than 1×10^7 cm^{-2}.

The top epilayer composition and degree of strain relaxation were determined with (400) and (422) x-ray rocking curves. Figure 2 shows a typical (400) x-ray spectrum. The constant background is due to the linearly graded buffer layer. All of the layers examined were almost completely relaxed (around 97%) along both in-plane ⟨011⟩ directions. For $x \approx 0.3$, a top layer growth temperature of 540 °C is optimal with respect to the x-ray linewidth. The smallest linewidth measured for a 1.4-μm-thick $In_{0.32}Ga_{0.68}P$ layer grown on a 1.2-mm-thick graded buffer layer was 500 arcsec.

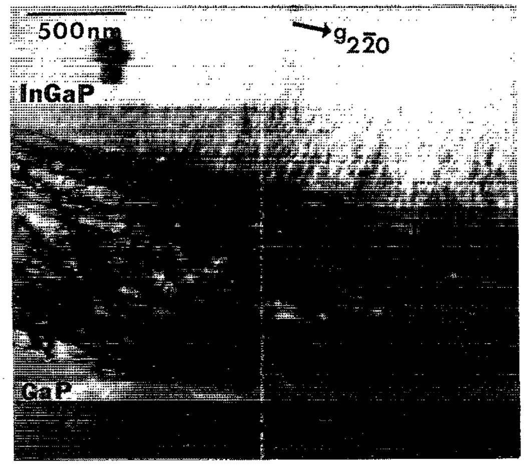

FIG. 1. Cross-section TEM micrograph of an $In_{0.32}Ga_{0.68}P$ epilayer grown on a linearly graded buffer layer on a GaP(100) substrate. The thickness of the linearly graded buffer is 1.15 μm.

Room-temperature PL measurements were performed on samples with different In compositions. The highest luminescence intensity was obtained at 584 nm from a layer with 32% indium. The emission efficiency was low for lower indium concentrations because the direct-indirect band-gap crossover occurs at $x \approx 0.28$. In the case of higher indium concentrations above 32%, the PL intensity also decreased probably due to the increasing lattice mismatch. Consistent with x-ray results, the 300 K PL intensity for $x \approx 0.32$ is about 30% higher for a growth temperature of 520–540 °C than 480 °C. Photoluminescence at lower tem-

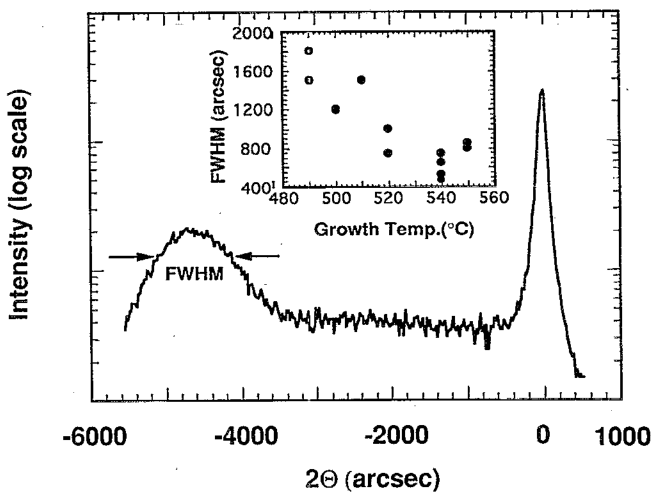

FIG. 2. (400) x-ray rocking curve of a 1.4-μm-thick $In_{0.3}Ga_{0.7}P$ layer grown on a linearly graded buffer layer on GaP(100). The insert shows the effect of growth temperature on the x-ray linewidth.

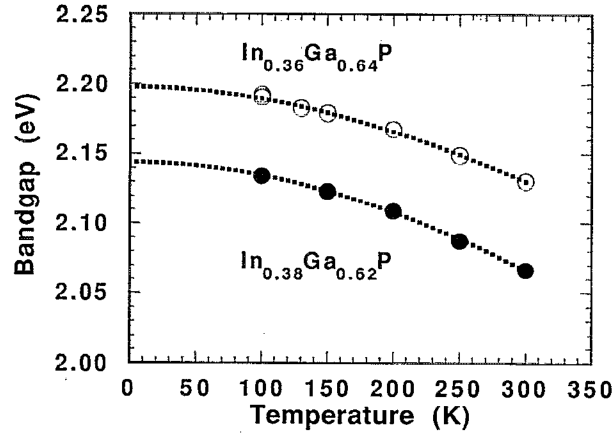

FIG. 3. Temperature dependence of the $In_xGa_{1-x}P$ band-gap energy measured by photoluminescence. The dashed line is the result of fitting with the Varshni equation.

peratures was also measured, and the relationship between the peak energy and temperature was fit with the Varshni equations (Fig. 3).[13] The extrapolated band-gap energy of $In_xGa_{1-x}P$ versus indium composition at 4.2 K is consistent with the theoretical band gap for a relaxed $In_xGa_{1-x}P$.[14]

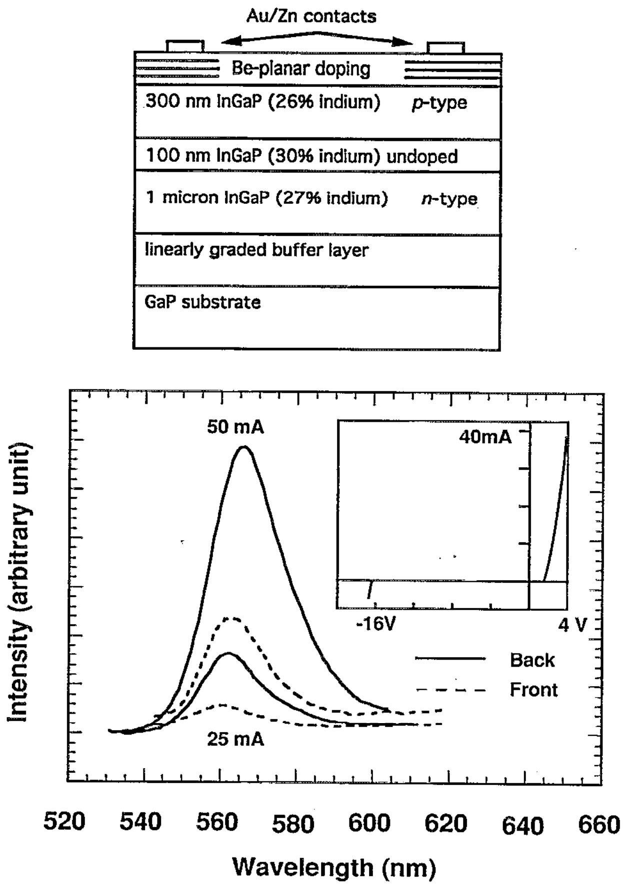

FIG. 4(a). Device structure of an $In_xGa_{1-x}P$ heterojunction LED. The dose for the Be planar doping is 5×10^{12} cm^{-2}. (b) Electroluminescence (EL) and *I-V* curve of the LED. The EL is measured at 25 and 50 mA from both the front side (dashed lines) and back side (solid lines).

Heterojunction $In_xGa_{1-x}P$ *p-i-n* diodes with electroluminescence (EL) at peak wavelengths 560–565 nm were fabricated. The structure is shown in Fig. 4(a). The 100 nm active layer and the *p*-type cap layers were grown pseudomorphically on a relaxed $In_{0.27}Ga_{0.73}P$ layer. The cap layer contained three Be-planar doping regions to reduce the contact resistance. The *I-V* characteristics showed a high breakdown voltage (≈ -16 V), and leakage currents less than 100 nA at -16 V despite the highly mismatched epilayer. However, a problem with this diode structure was the high series and contact resistance due to the difficulty in achieving high *p*-type doping in $In_xGa_{1-x}P$.[3] Although the Be planar doping in the ohmic contact layer (dose of each plane $\approx 5\times10^{12}$ cm^{-2}) reduced the contact resistance from 4.5×10^{-3} to 3×10^{-3} Ω cm^2 compared to a uniformly doped contact layer, poor current spreading results in light blocked by the metal contact when EL measurements are performed from the front side [dashed lines, Fig. 4(b)]. Light emission measured from the back side is improved by about a factor of 2 [solid lines, Fig. 4(b)] because the GaP substrate is transparent. Device geometry and the processing shall be further optimized to maximize light extraction.

In summary, we have demonstrated that a compositionally graded buffer can effectively reduce the number of threading dislocations in the $In_xGa_{1-x}P$/GaP system to obtain materials potentially useful for visible light emitting applications. X-ray and PL data show that the epilayer grown on a linearly graded buffer layer is fully relaxed, with a threading dislocation density less than 1×10^7 cm^{-2}. Green LEDs (560 nm) with good rectifying and reverse breakdown characteristics were fabricated.

This work is supported by the Office of Naval Research and the National Science Foundation Presidential Young Investigator Award.

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