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Amber-green light-emitting diodes using order-disorder Al\textsubscript{x}In\textsubscript{1-x}P heterostructures

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We demonstrate amber-green emission from Al\textsubscript{x}In\textsubscript{1-x}P light-emitting diodes (LEDs) with luminescence peaked at 566 nm and 600 nm. The LEDs are metamorphically grown on GaAs substrates via a graded In\textsubscript{0.5}Ga\textsubscript{0.5}As buffer layer and feature electron confinement based on the control of Al\textsubscript{x}In\textsubscript{1-x}P CuPt atomic ordering. A control sample fabricated without order-disorder carrier confinement is used to illustrate device improvement up to a factor of 3 in light output due to confinement at drive currents of 40 A/cm\textsuperscript{2}. The light output at room temperature from our Al\textsubscript{x}In\textsubscript{1-x}P LED structure emitting at 600 nm is 39\% as bright as a Ga\textsubscript{0.5}In\textsubscript{0.5}P LED emitting at 650 nm. © 2013 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4818477]

I. INTRODUCTION

While recent commercial development of solid-state lighting (SSL) has been focused on phosphor down-converted architectures using III-nitride light-emitting diodes (LEDs), direct color-mixed architectures for SSL retain a high level of technological appeal due to their potential advantages in increased energy savings and flexible tuning of the color point for “smart lighting” applications.\textsuperscript{1,2} In order to attain good color rendering in a color-mixed LED lamp featuring narrow-band light emitters, four colors are needed in the red, amber, green, and blue; optimal wavelength targets of 459 nm, 535 nm, 573 nm, and 614 nm have been suggested.\textsuperscript{3} The amber and green targets provide the greatest material challenge and opportunity for improvement, due to limited performance of established In\textsubscript{0.5}Ga\textsubscript{0.5}As and (Al\textsubscript{0.5}Ga\textsubscript{0.5})\textsubscript{0.51}In\textsubscript{0.49}P material systems at these wavelengths.\textsuperscript{4,5} In this technological context, novel material systems with emission in the amber-green wavelength range (560–595 nm) are particularly relevant.

We demonstrate the feasibility of fabricating LEDs featuring direct bandgap emission at 566 nm and 600 nm using Al\textsubscript{x}In\textsubscript{1-x}P LED structures. The ternary alloy Al\textsubscript{x}In\textsubscript{1-x}P has the highest direct bandgap of any material in the conventional (non-nitride) III–V semiconductor alloy system\textsuperscript{6} with a direct-indirect crossover near 2.3 eV,\textsuperscript{7} making it a natural candidate for light emission in the amber and yellow-green regions of the spectrum. However, optoelectronic devices using Al\textsubscript{x}In\textsubscript{1-x}P have not yet been broadly explored in the literature. One reason for the relative scarcity of research on Al\textsubscript{x}In\textsubscript{1-x}P devices is the lack of a convenient substrate for strain-free growth of direct-bandgap Al\textsubscript{x}In\textsubscript{1-x}P. The direct bandgap regime occurs for aluminum concentrations \(x \approx 0.44 – 0.49\)\textsuperscript{2,4} with lattice mismatch of >1\% relative to GaAs. The range of values cited for this crossover illustrates a considerable uncertainty in reported literature values regarding the dependence of the direct bandgap on \(x\). Reported device studies include low-temperature band-alignment measurements on Al\textsubscript{x}In\textsubscript{1-x}P/(Al\textsubscript{0.5}Ga\textsubscript{0.5})\textsubscript{0.51}In\textsubscript{0.49}P heterostructures\textsuperscript{8} and strained quantum-well lasers emitting at 650 nm.\textsuperscript{9} In this work, we utilize an In\textsubscript{0.5}Ga\textsubscript{0.5}As compositionally-strained quantum-well laser system\textsuperscript{10} to achieve virtual substrates at the appropriate lattice constants for growth of Al\textsubscript{x}In\textsubscript{1-x}P films and devices in the direct bandgap regime. This technique has the advantage of allowing strain relaxation during buffer growth, leading to low threading dislocation densities in the optically active material above.

Inspired by the traditional double-heterostructure design of high-brightness (Al\textsubscript{0.5}Ga\textsubscript{0.5})\textsubscript{0.51}In\textsubscript{0.49}P LEDs,\textsuperscript{12} spontaneous CuPt atomic ordering can be used to create disordered cladding layers for electron confinement in an ordered active layer of Al\textsubscript{x}In\textsubscript{1-x}P. The crucial role of spontaneous atomic ordering in determining the electronic structure of Al\textsubscript{x}In\textsubscript{1-x}P has been considered in recent studies.\textsuperscript{9,13} This phenomenon has also been studied extensively in the Ga\textsubscript{0.5}In\textsubscript{0.5}As material system.\textsuperscript{14,15} Lee et al. demonstrated an order-disorder heterostructure LED using Ga\textsubscript{0.5}In\textsubscript{0.5}As in 1992.\textsuperscript{16} Recently, Tang et al.\textsuperscript{17} have also demonstrated the growth of unicompositional order-disorder heterostructures in Al\textsubscript{x}In\textsubscript{1-x}P. In this work, we have characterized the direct bandgap shift due to ordering in several epitaxial Al\textsubscript{x}In\textsubscript{1-x}P films under a variety of growth conditions and have fabricated LEDs using the order-disorder confinement strategy with high-quality direct-bandgap Al\textsubscript{x}In\textsubscript{1-x}P.

II. EXPERIMENTAL PROCEDURE

The devices studied in this report are double-heterostructure LEDs as illustrated schematically in Figure 1(a). In addition, several Al\textsubscript{x}In\textsubscript{1-x}P films were also grown under various conditions to explore the growth regime most conducive to atomic ordering. The Al\textsubscript{x}In\textsubscript{1-x}P devices and films reported here were all grown on compositionally-strained In\textsubscript{0.5}Ga\textsubscript{0.5}As on GaAs substrates. Epitaxy was performed in a Thomas Swan/AIXTRON low-pressure metalorganic chemical vapor deposition (MOCVD) reactor with
while the active region was grown at 650°C.

The growth pressure was fixed at 100 Torr and purified used as the group V precursors. The V/III ratio was fixed at 420. The growth temperature and doping properties of the active and cladding layers are indicated. (c) Transmission electron diffraction images show that both variants of CuPt-B type ordering occur in the active layer but ordering is suppressed in the cladding layers.

 buffers were grown at a lattice mismatch grading rate of 0.7 μm with the composition linearly graded by computer controlled mass flow controllers. The graded buffer was capped with a final InGaAs layer of constant composition, 0.7 μm thick. AlInP was initiated by immediately switching on the TMAl and PH3 sources and turning off the TMGAs and AsH3 sources. The aluminum composition in the AlInP devices and films was controlled by calibrated flow rates of the precursor gases, and subsequently estimated by x-ray diffraction reciprocal space maps of the (400) diffraction peak. This method allows determination of x with an experimental uncertainty of ±0.01. The bulk epilayer films studied here have an aluminum concentration x = 0.33, while the reported devices have larger aluminum fractions x = 0.36 and x = 0.39.

For devices, the cladding layers were grown at 725°C, while the active region was grown at 650°C to promote ordering. Typical doping concentrations of the n-type Si-doped and p-type Zn-doped cladding layers were 10¹⁹ cm⁻³ and 10¹⁸ cm⁻³, respectively. Devices were post-growth annealed for 60 s at 425°C in a rapid thermal annealer under argon atmosphere with GaAs proximity caps in order to activate the Zn dopants. Electrical contacts were formed by electroplating gold. An InGaAs cap, used to improve ohmic contacts at the p-side, was subsequently etched away using the front-surface gold contact grid as a mask.

Three different AlInP LEDs are included in this report, with properties summarized in Table I. Devices 1 and 2 were grown on substrates with surface miscut 6°C/14 to promote CuPt atomic ordering so that device 2B provides a completely disordered control to check the effectiveness of cladding in device 2. The growth conditions were optimized for the miscut 6A growth, leading to a difference in material quality between devices 2 and 2B that was duly considered in the analysis. The primary differences between devices 1, 2, and 2B are the aluminum composition fraction and the degree of ordering in the active region, leading to different emission peak wavelengths. Devices 2 and 2B have active region thickness of approximately 300 nm, while device 1 has an active region thickness of approximately 400 nm.

A reference device featuring a GaInAsP active region between (Al0.6Ga0.4)0.51In0.49P cladding layers was also grown on a miscut 6A GaAs substrate. This reference device was chosen as the brightest among several GaInAsP LEDs grown under similar conditions to the AlInP devices, and thus provides a comparison point to gauge the relative performance of the AlInP LEDs.

Photoluminescence (PL) measurements were performed using a 452 nm continuous wave solid-state laser and an Andor Shamrock 0.5 m spectrometer calibrated with a neon discharge lamp. Electroluminescence (EL) spectra were collected using a TRIAX 320 spectrometer (0.32 m focal length), also calibrated with a neon discharge lamp. Angle-integrated electroluminescence intensity was gathered using a commercially-available integrating sphere LCS-100 system from Labsphere. Current-voltage characteristics and EL spectra were collected under steady current drive conditions, using a Keithley 220 or Keithley 2400 current source. Voltages were measured using a Keithley 6514 system electrometer in a four-point measurement configuration. Integrated light output measurements were conducted under pulsed current drive with a pulse length of 200 μs and 1% duty cycle in order to mitigate the effects of device self-heating.

III. RESULTS AND DISCUSSION

A. Atomic ordering of AlInP

Almost all ternary and quaternary III–V alloys are known to spontaneously form CuPt-type ordering domains. A useful summary of CuPt ordering in GaInAsP is provided in the introduction to optical spectroscopy work by Ernst et al.14 and details on historical developments in the

<table>
<thead>
<tr>
<th>Device</th>
<th>Substrate</th>
<th>Al fraction, x</th>
<th>EL peak (300 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device 1</td>
<td>Miscut 6A</td>
<td>0.39</td>
<td>566 nm</td>
</tr>
<tr>
<td>Device 2</td>
<td>Miscut 6A</td>
<td>0.36</td>
<td>600 nm</td>
</tr>
<tr>
<td>Device 2B</td>
<td>(111)B</td>
<td>0.36</td>
<td>586 nm</td>
</tr>
</tbody>
</table>
study of spontaneous ordering in several semiconductor alloys are described in the 2002 review collection edited by Mascarenhas.\textsuperscript{15} In the case of Al\textsubscript{x}In\textsubscript{1-x}P, CuPt-B type atomic ordering is manifested when the aluminum and indium sublattices spontaneously segregate into alternating aluminum-rich and indium-rich (111) planes of the crystal structure. For partially-ordered Al\textsubscript{x}In\textsubscript{1-x}P, an order parameter \( \eta \) is defined by the statement that the aluminum (111) planes have aluminum fraction \( x + \eta/2 \) and the indium-rich (111) planes have aluminum fraction \( x - \eta/2 \). From this definition, it is clear that \( \eta = 0 \) in a fully-disordered (random) alloy. The maximum possible degree of ordering depends on \( x \), with the case \( \eta = 1 \) occurring only for fully-segregated aluminum and indium sublattices when \( x = 0.5 \). The bandgap energy is expected to be highest in fully-disordered alloys, with increased ordering leading to a bandgap decrease due primarily to a downward motion of the conduction band, as described by Wei and Zunger.\textsuperscript{19} Hence, the bandgap energy of Al\textsubscript{x}In\textsubscript{1-x}P alloys is determined by both the composition and the degree of spontaneous ordering that occurs during alloy growth, with the dependence on \( \eta \) given by\textsuperscript{19}

\[
E_g(x, \eta) = E_g(x, 0) + \eta^2 [E_g(x, 1) - E_g(x, 0)].
\] (1)

As an illustration of the bandgap shifts due to CuPt atomic ordering in this material system, we present the results of PL measurements on several Al\textsubscript{x}In\textsubscript{1-x}P films all with similar composition, \( x = 0.33 \). Figure 2 shows the as-grown PL spectra of three example films at various growth temperatures, showing a wide distribution of peak emission wavelengths attributed to different degrees of atomic ordering. In order to confirm this attribution, each of the above samples was subsequently annealed at 925 °C for 60 s. This process of high-temperature annealing has been shown by Tang \textit{et al.} to remove internal atomic ordering of the material after growth.\textsuperscript{20} After the high-temperature anneal, all of the Al\textsubscript{0.33}In\textsubscript{0.67}P films showed PL spectra with a shifted emission peak near 2.10 eV; one of these post-anneal spectra is also shown in Figure 2. The energy of the post-anneal emission peak is consistent with the expected direct bandgap for completely disordered Al\textsubscript{x}In\textsubscript{1-x}P at \( x = 0.33 \) according to the relationship \( E_g = 1.35 + 2.23x \) determined by Onton and Chicotka\textsuperscript{7} from melt-grown Al\textsubscript{x}In\textsubscript{1-x}P ingots that certainly did not feature any atomic ordering. The agreement among the post-annealed PL peak energies and the expected bandgap value for disordered Al\textsubscript{0.33}In\textsubscript{0.67}P indicates that the redshifts in bandgap of the as-grown PL spectra are due to atomic ordering during the growth of the films. The samples shown in Figure 2 have emission peaks that are 27, 151, and 277 meV, respectively, below the disordered bandgap energy.

The largest redshift encountered during this investigation was spectrum (a) in Figure 2, corresponding to a film grown on a miscut 4A substrate (4° miscut towards \((-1\text{-}1\text{-}1)\text{A}\) from (100)). Electroreflectance measurements confirmed direct bandgap energies consistent with the observed PL peak locations before and after high-temperature annealing on this sample. While the majority of this work has focused on growth on miscut 6A substrates, it is useful to note that miscut 4A substrates may offer yet higher achievable degrees of atomic ordering. The dependence of atomic ordering degree on substrate orientation has been studied in detail for the Ga\textsubscript{x}In\textsubscript{1-x}P material system, with maximal \( \eta \) reported\textsuperscript{31} for miscut angle between 3° and 6°. Several other factors are also known to affect the degree of spontaneous atomic ordering during material growth, including growth temperature,\textsuperscript{32} growth rate,\textsuperscript{23} V/III ratio,\textsuperscript{22} and dopant incorporation.\textsuperscript{24,25}

The effect of growth temperature on the measured bandgap shift due to atomic ordering is explored in Figure 3. The bandgap shifts shown here are each determined by comparing as-grown PL peak position, \( E_{PL\text{peak}} \), to disordered material peak position, \( E_g(\eta = 0) \), exactly analogous to the redshifts calculated for Figure 2. For consistency, all data points are from films with a composition \( x = 0.33 \) grown on miscut 6A substrates, with constant V/III ratio and no doping. The largest redshift that was achieved at each growth temperature is plotted, since uncontrollable factors such as growth reactor cleanliness and history can also cause a significant decrease in atomic ordering. Assuming a simple linear decrease in \( \eta \) as temperature changes away from the optimal ordering temperature, these bandgap shifts can be fit to an inverted parabola corresponding to \( \Delta E_g \propto \eta^2 \). This
model indicates that the optimal growth temperature for ordering is 680°C; outside the range of 600°C-760°C, little to no ordering is expected. The bandgap shift due to ordering at optimal growth temperature is estimated at 180 meV for the growth conditions explored here (miscut 6A substrate, x = 0.33 and V:III ratio = 420). By way of comparison, a similar exploration from Jinghua et al.13 using different growth conditions (on-axis substrate, x = 0.42 and V:III ratio = 40) found 660°C to be the optimal growth temperature for ordering of Al1–xInxP, with similar values of expected bandgap shift.

Control of ordering within our device structure is achieved by a combination of growth temperature adjustment and dopant incorporation, informed by ongoing growth studies of this material system26 along the lines reported above. Ordering is encouraged during the active layer growth by using a growth temperature of 650°C and suppressed during the cladding layer growth by elevating the growth temperature to 725°C as well as by the high dopant incorporation rate. Figure 1(b) shows a transmission electron micrograph (TEM) image of a typical Al1–xInxP device successfully implementing the order-disorder heterostructure design, aligned with the schematic layer descriptions in Figure 1(a). Color contrast stripes weakly visible within the active layer are attributed to composition modulation of the Al1–xInxP film.26 Figure 1(c) shows representative transmission electron diffraction (TED) images from each cladding layer and from the active region of the device. The superspots visible in the active region TED image indicate the presence of both variants of CuPt-B ordering. In the cladding layers, these superspots are absent from the TED images, indicating a disordered (random) alloy in these regions.

Based on the reported results for bulk epilayer Al1–xInxP films, we anticipate that bandgap differences between cladding and active layers in excess of 150 meV can be achieved by optimizing our control of material ordering. For LED devices 1 and 2 reported in this work, bandgap shift due to ordering is estimated at 20-60 meV. Hence, the order-disorder heterostructure device strategy used here provides a clear opportunity for future LED improvements.

### B. Al1–xInxP LED characteristics

The current-voltage (I–V) characteristics of devices 1 and 2 were measured using a device geometry having a mesa area of 0.01 cm² to allow for high drive current densities. The resulting I–V curves for each device are plotted in Figure 4. Both devices show exponential behavior with an ideality factor of n = 2, consistent with dominant carrier recombination in the depletion region. At very low or high drive currents, the I–V behavior is dominated by parasitic effects. The shunt resistance for device 1 is estimated to be 200 MΩ, and a sub-threshold turn-on of diode current is also visible just below the exponential regime. The series resistance for device 1 is estimated to be 7 Ω. Deviations from the ideal diode behavior, including sub-threshold turn-on in both devices and additional parasitic losses at high current density in device 2, indicate areas for improvement in future device optimizations.

As an inset to Figure 4, the EL emission at room temperature from each device is shown in a photograph taken at a drive current of 0.1 A/cm². The light emission is a uniform amber or green across the mesa area; the dark grid pattern is due to light blocked by the patterned gold contact on the front surface of each LED. The EL spectra from devices 1 and 2 as well as the Ga0.51In0.49P reference LED were also measured at 300 K using a device geometry with a mesa area of 0.1 cm² and a drive current density J = 1 A/cm². These spectra are shown in Figure 5. The 566 nm and 600 nm emitting Al1–xInxP devices have integrated EL spectra that are 23% and 39%, respectively, as bright as the Ga0.51In0.49P reference device. The performance of the Al1–xInxP devices relative to a similar-quality, unoptimized Ga0.51In0.49P device strongly indicate that an Al1–xInxP material system holds promise for effective light emission in the amber-green wavelength range.
In order to explore the effectiveness of the order-disorder cladding structure, device 2B was grown simultaneously with device 2 using an alternate substrate of (111)B GaAs to inhibit ordering of AlInP in the active region. Hence, device 2 and device 2B have the same device structure, allowing for a reasonably controlled investigation of the order-disorder confinement effectiveness. Since growth conditions were optimized for the miscut 6A growth of device 2, the material quality of device 2B is not as good as for device 2, and device 2B is significantly dimmer. Therefore, Figure 6 shows the integrated light output after normalizing each device to its own performance at a drive current of 1 A/cm². This normalization removes the contribution of material quality effects, and emphasizes the difference in slope between the two devices. Relative to device 2, device 2B shows less light output at high current drives, consistent with a device showing poor carrier confinement. This preliminary analysis indicates that the order-disorder heterostructure is indeed improving LED performance in our AlInP LEDs, as expected. The magnitude of the cladding improvement is a factor of 3 in total light output at 40 A/cm² drive current density.

IV. CONCLUSION

We have demonstrated direct-bandgap AlInP LEDs with room-temperature emission in the amber-green spectral range at 566 nm and 600 nm. These devices achieve cladding for electron confinement via controlled order-disorder heterostructures. Comparison of light output at 40 A/cm² indicated a factor of 3 improvement in LED performance due to the electron confinement. AlInP LED light output can be up to 39% as bright as a reference Ga0.51In0.49P device, where commercially produced Ga0.51In0.49P LEDs are known to achieve LED external quantum efficiencies of at least 55%.1 We have also shown bandgap differences of over 150 meV due to ordering in bulk epilayer AlInP films, indicating the potential for future improvement of AlInP LED performance using this confinement strategy. Hence, direct-bandgap AlInP holds promise as a future light-emitter to access the amber-green spectral regime that is essential for direct color-mixing applications in the LED lighting industry.

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