650-nm AlGaInP multiple-quantum-well lasers grown by metalorganic chemical vapor deposition using tertiarybutylphosphine

Jian-Rong Dong,[a] Jing-Hua Teng, Soo-Jin Chua,[b] Boon-Chin Foo, Yan-Jun Wang, and Hai-Rong Yuan
Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602

Shu Yuan
School of Materials Engineering, Nanyang Technological University, Singapore 639798

(Received 14 January 2003; accepted 20 May 2003)

Using tertiarybutylphosphine (TBP) as phosphorus precursor, high-quality AlGaInP epilayers and AlGaInP/GaInP multiple-quantum-well (MQW) structures have been grown by metalorganic chemical vapor deposition. The photoluminescence results indicate that the AlGaInP materials are as good as those grown using PH_3 in terms of optical quality. Finally, AlGaInP MQW red laser structures have been grown, and the electrically pumped AlGaInP red lasers grown by TBP have been demonstrated with the emission wavelength of 647 nm, indicating that TBP can be used to grow high-quality AlGaInP epilayers and AlGaInP-based red lasers, which presently is dominated by the highly toxic gas source PH_3.
[DOI: 10.1063/1.1593782]

Since the emergence of CW red lasers based on the AlGaInP material in 1985,[1–3] AlGaInP semiconductor red lasers have attracted a lot of research attention due to their wide applications, such as in color printers, barcode readers, digital versatile disk drivers, and so on. Most of the AlGaInP lasers are grown using PH_3 as a phosphorus source by either metalorganic chemical vapor deposition (MOCVD) or gas source molecular-beam epitaxy. Because of the high toxicity of PH_3, a substitute source for PH_3 has been sought after. Tertiarybutylphosphine (TBP) has been considered a promising P precursor for material growth, and work has been carried out to understand the decomposition process of TBP.[4,5] Compared with PH_3, TBP has advantages as a P precursor, it is much safer due to the lower vapor pressure and several orders of magnitude lower toxicity,[6] and has lower decomposition temperature,[4] which is useful for suppressing the diffusion of dopants in device structures where an abrupt doping profile is critical to the performance of the devices. Using TBP, high-mobility InP and high-quality semi-insulating InP epilayers have been grown by MOCVD,[7–9] also high-quality InGaAsP quantum well long wavelength lasers grown by TBP and tertiarybutylarsine (TBAs) have been demonstrated.[10,11] However, when it comes to the case of AlGaInP material, although some research groups have used TBP as an alternative source to grow AlGaInP,[12–16] only AlGaInP red-light-emitting diodes have been realized.[15] So far, the attempts to grow AlGaInP red lasers have not been successful due to lower quality of AlGaInP epilayers. Compared with InGaAsP, AlGaInP is more sensitive to the impurity oxygen in the TBP and the growth of AlGaInP is a more severe test on the quality of TBP. With the improvement in purity of TBP source and the optimization of the growth conditions, the realization of red AlGaInP lasers grown by TBP is becoming increasingly possible.

In this letter, AlGaInP multiple-quantum-well (MQW) red lasers grown with TBP have been demonstrated. High-quality AlGaInP epilayers were grown by low-pressure MOCVD using TBP as P precursor, and then, by optimizing growth conditions, AlGaInP MQW laser structures have been grown and processed into broad-area lasers. Electroluminescence measurements demonstrated that lasing has been obtained from AlGaInP QWs. This report on AlGaInP red laser grown using TBP indicates that the less toxic metalorganic source TBP can be used for growth of Al-containing phosphide and related device structures.

All the material growths were performed employing a low-pressure horizontal MOCVD system with planetary rotation to ensure the uniformity of the grown materials. AlGaInP epilayers were grown on n^+-GaAs substrates with the orientation of (100) 7° off towards (111)A to suppress the spontaneous ordering in the (Al)GaInP epilayers.[17] Trimethylgallium, trimethylindium, and trimethylaluminum were used as group III sources, and TBAs and TBP were utilized as the group V sources. SiH_4 and diethylzinc were used for the *n*- and *p*-type doping, respectively. The growth temperature was 675 °C as measured by a thermocouple inserted in the graphite susceptor. The growth chamber pressure was set at 100 mbar. The V/III ratio was 75 and the growth rate was about 1 μm/h. Prior to the growth of AlGaInP, a 150-nm GaAs buffer layer was grown. Philips X'pert™ high-resolution x-ray diffraction was used to determine the lattice mismatch between the epilayers and the GaAs substrate and to measure the layer thickness. The optical properties of AlGaInP were characterized by photoluminescence (PL) both at low and room temperatures. For the low-temperature (LT) (14 K) measurements, the samples were mounted on a cold finger of a closed cycle He cryostat. The 488-nm line of an Ar^+ laser was used as the excitation

[a]Electronic mail: jr-dong@imre.a-star.edu.sg
[b]Electronic mail: elecsj@nus.edu.sg

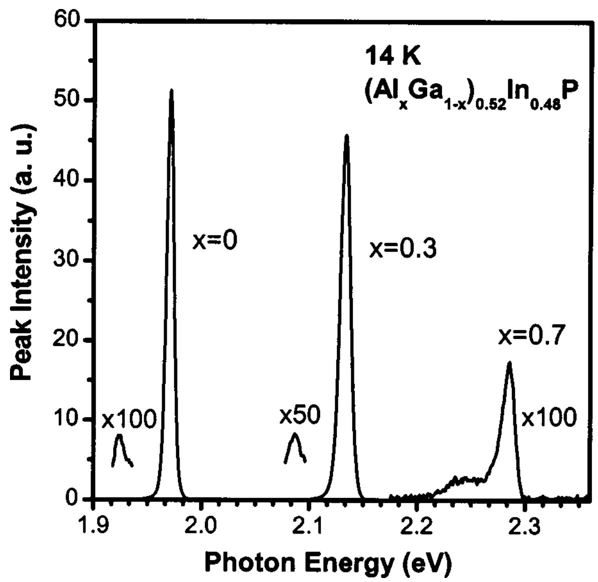

FIG. 1. LT PL spectra of AlGaInP epilayers grown using TBP.

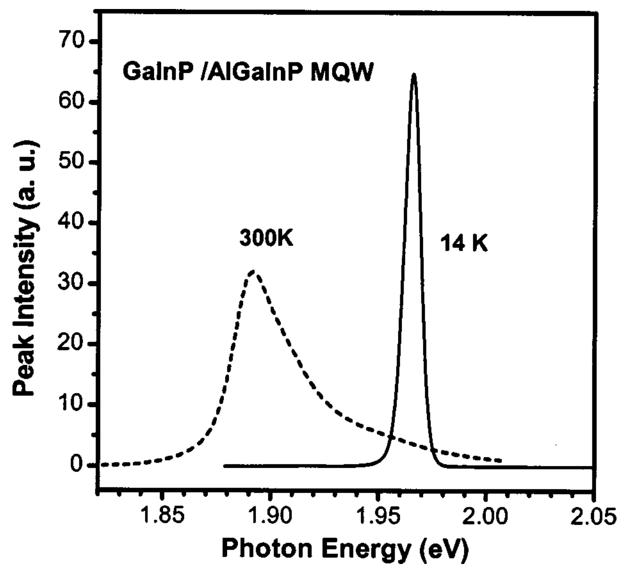

FIG. 2. PL spectra of a four-period GaInP (8 nm)/AlGaInP (10 nm) QW structure at RT and LT.

source and the emissions were collected by lenses and dispersed by a 0.75-m monochromator, and then detected using a cooled photomultiplier tube. A standard lock-in technique was employed to increase the signal-to-noise ratio. RT PL measurements were performed on an Accent RPM 2000 system, excited by the 532-nm line of a Kr laser at 11 mW.

GaInP was first grown lattice-matched to GaAs substrate, and AlGaInP was subsequently grown by introducing Al source while Ga source flow rate was reduced correspondingly to keep the AlGaInP lattice matched to GaAs substrates. In the following discussion, all the TBP-grown AlGaInP epilayers are about 430 nm thick.

Figure 1 shows the LT PL spectra of AlGaInP epilayers of different Al compositions. From the spectra, we can see narrow band edge emission peaks without any other defect or impurity related peaks as observed in Ref. 18. The full width at half-maximum (FWHM) of $Ga_{0.52}In_{0.48}P$, $(Al_{0.3}Ga_{0.7})_{0.52}In_{0.48}P$, and $(Al_{0.7}Ga_{0.3})_{0.52}In_{0.48}P$ PL spectra are 7.5, 10, and 16.7 meV, respectively. The corresponding FWHMs for AlGaInP grown using PH_3 not shown here, are 5.8, 11, and 17 meV, respectively. These results suggest the good quality of the AlGaInP epilayers grown using TBP. In the case of $(Al_{0.7}Ga_{0.3})_{0.52}In_{0.48}P$, another significant peak at lower energy side can be seen, the energy difference between the dominant peak and the low-energy peak is about 47 meV. The peak cannot be attributed to the impurities Si or Zn, which are doping sources in our MOCVD system, because the ionization energies of Si and Zn in AlGaInP are about 10 and 44 meV, respectively.[19,20] For $x=0.7$, $(Al_xGa_{1-x})_{0.52}In_{0.48}P$ becomes an indirect band-gap material. The main peak can be attributed to recombination near indirect band edge. In indirect band-gap materials, the phonon replicas are more likely to be observed, therefore, the lower energy peaks probably originate from the phonon replica of the main peak because the energy difference between the main peak and the weak peak agrees fairly well with the energies of LO phonons in AlGaInP.[21–23] For $Ga_{0.52}In_{0.48}P$ and $(Al_{0.3}Ga_{0.7})_{0.52}In_{0.48}P$, very weak low-energy peaks are similarly observed, as shown in Fig. 1, with an energy difference of some 47 meV between the weak peak and the respective main peak. Likewise, the low energy peaks can be ascribed to the LO phonon replicas.[24] The observation of phonon replica in GaInP suggests the high quality of GaInP epilayers grown by TBP. In (Al)GaInP epilayers grown using PH_3, similar low-energy peaks are also observed.

Figure 2 shows the LT and RT PL spectra of $Ga_{0.49}In_{0.51}P$ (8 nm)/$(Al_{0.4}Ga_{0.6})_{0.52}In_{0.48}P$ (10 nm) four-quantum-well structure. The FWHMs are 7.7 and 35 meV for LT and RT, respectively. The narrow line widths indicate good optical quality of the structures. Comparison of the PL intensities at LT and RT does not make sense because we used different systems for LT and RT PL measurements.

The MQW laser structure consists of the following layers: starting from n^+-GaAs substrate, 200-nm Si-doped GaAs buffer layer ($n \cong 2\times10^{18}$ cm^{-3}), 60-nm Si-doped GaInP transition layer ($n \cong 2\times10^{18}$ cm^{-3}), 800-nm Si-doped n-$(Al_{0.7}Ga_{0.3})_{0.52}In_{0.48}P$ cladding layer ($n \cong 2\times10^{18}$ cm^{-3}), 30-nm undoped $(Al_{0.7}Ga_{0.3})_{0.52}In_{0.48}P$ cladding layer, 80-nm undoped $(Al_{0.4}Ga_{0.6})_{0.52}In_{0.48}P$ layer, 3-period $Ga_{0.49}In_{0.51}P$ (8 nm)/$(Al_{0.4}Ga_{0.6})_{0.52}In_{0.48}P$ (10 nm) QW active layers, 80-nm undoped $(Al_{0.4}Ga_{0.6})_{0.52}In_{0.48}P$ layer, 50-nm undoped $(Al_{0.7}Ga_{0.3})_{0.52}In_{0.48}P$ layer, 1200-nm Zn-doped p-$(Al_{0.7}Ga_{0.3})_{0.52}In_{0.48}P$ cladding layer ($n \cong 1\times10^{18}$ cm^{-3}), 100-nm Zn-doped GaInP transition layer ($p \cong 2\times10^{18}$ cm^{-3}), and 150-nm Zn-doped GaAs contact layer ($p \cong 1\times10^{19}$ cm^{-3}). Broad contact lasers were fabricated to test the quality of the materials grown by TBP. First, a dielectric film SiO_2 of 200-nm-thick was deposited on the wafer by plasma-enhanced chemical vapor deposition, and a window 15 μm wide was then opened up using photolithography. Pd/Ti/Pd/Au metal layers were e-beam evaporated on the top of the wafer for a p-type contact. Subsequently, the wafer was thinned to some 100 μm by mechanical polishing followed by the evaporation of AuGe/Ni/Au for an n-type ohmic contact. Annealing at 450 °C was performed to form ohmic contacts. Finally, the wafer was cleaved and tested at RT without facet coatings and heat sinking using a current injection with pulse width of 2 μs and duty cycle of 1%. Through an objective lens, the laser emission was focused

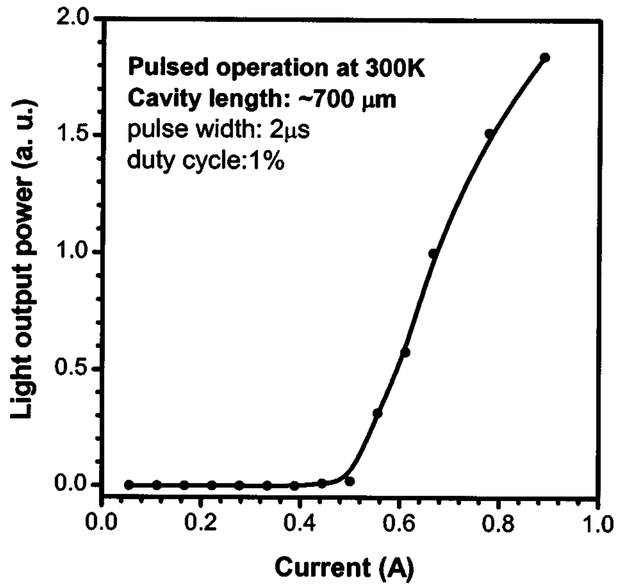

FIG. 3. Light output power versus current characteristics of an AlGaInP MQW laser.

and coupled to a 3-m-long optical fiber by which the light is guided to an ANDO optical spectrum analyzer where the spectrum is measured and recorded. The wavelength resolution is 0.015 nm.

The laser light output power versus injection current ($L-I$) curve is given in Fig. 3. As can be seen, the threshold current I_{th} is about 500 mA, corresponding to a current density of about 5 kA/cm^2. Figure 4 shows the laser spectrum of an AlGaInP MQW laser at an injection current of $1.2I_{th}$. Although multiple longitudinal modes are observed when the injection current is above the threshold, which is the typical characteristics of Fabry–Perot cavity lasers, one mode at 647.3 nm is much stronger. The linewidth of the dominant mode is about 0.2 nm, clearly indicating the lasing of the

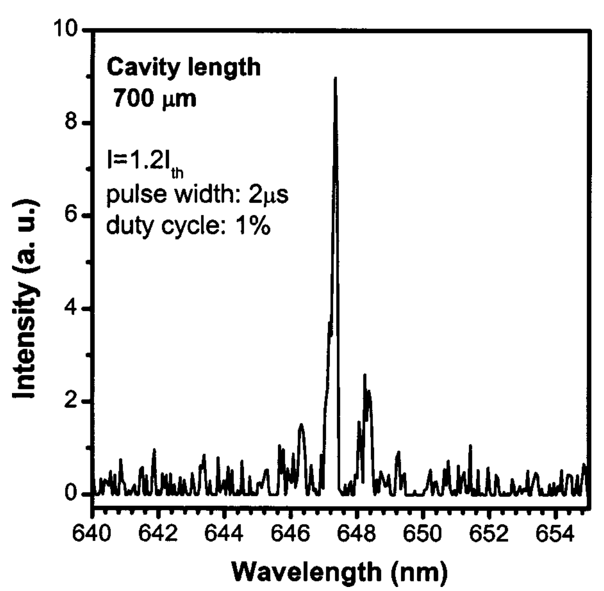

FIG. 4. Emission spectrum of a typical AlGaInP MQW Fabry–Perot laser under pulsed current injection.

device. Without lateral carrier confinement, the absence of the facet coatings and the lack of an efficient heat sink to effectively extract the heat generated in the chip during operation, the laser can only operate under pulse injection conditions. To achieve CW operation, further optimizing the material growth conditions, fabricating ridge waveguide, coating the facets and mounting the chips on a heat sink are in progress.

In summary, AlGaInP epilayers and MQW structures have been grown by MOCVD using TBP, and the materials have been characterized by PL measurements. The narrow PL line widths of AlGaInP epilayers and GaInP/AlGaInP MQW structures suggest that high optical quality AlGaInP epilayers can be grown using TBP. Based on these results, AlGaInP/GaInP MQW laser structures were grown and broad-area lasers were fabricated. For the first time, AlGaInP MQW red lasers grown by TBP have been demonstrated. Therefore, one more choice now becomes available for the growth of high-quality AlGaInP materials and related devices.

The authors would like to thank L. Wishwanath for her assistance in the laser spectrum measurements.

[1] M. Ikeda, Y. Mori, H. Sato, K. Kaneko, and N. Watanabe, Appl. Phys. Lett. **47**, 1027 (1985).
[2] M. Ishikawa, Y. Ohba, H. Sugawara, M. Yamamoto, and T. Nakanisi, Appl. Phys. Lett. **48**, 207 (1986).
[3] K. Kobayashi, S. Kawata, A. Gomyo, I. Hino, and T. Suzuki, Electron. Lett. **21**, 931 (1985).
[4] S. H. Li, C. A. Larsen, N. I. Buchan, G. B. Stringfellow, W. P. Kosar, and D. W. Brown, J. Appl. Phys. **65**, 5161 (1989).
[5] C. W. Hill, G. B. Stringfellow, and L. P. Sadwik, J. Electron. Mater. **24**, 731 (1995).
[6] G. B. Stringfellow, in *Organometallic Vapor-Phase Epitaxy* (Academic, San Diego, 1989), p. 29.
[7] R. R. Saxena, J. E. Fouquet, V. M. Sardi, and R. L. Moon, Appl. Phys. Lett. **53**, 304 (1988).
[8] T. Imori, T. Ninomiya, K. Ushhikubo, and K. Kondoh, Appl. Phys. Lett. **59**, 2862 (1991).
[9] R. T. Huang, A. Appelbaum, D. Renner, and S. W. Zehr, Appl. Phys. Lett. **58**, 170 (1991).
[10] A. Ougazzaden, A. Mircea, R. Mellet, G. Primot, and C. Kazmierski, Electron. Lett. **28**, 1078 (1992).
[11] M. E. Heimbuch, A. L. Holmes, Jr., M. P. Mack, S. P. DenBaars, L. A. Coldren, and J. E. Bowers, Electron. Lett. **29**, 340 (1993).
[12] D. S. Cao and G. B. Stringfellow, J. Electron. Mater. **20**, 97 (1991).
[13] M. Mannoh, A. Ishibashi, and K. Ohnaka, J. Cryst. Growth **145**, 158 (1994).
[14] T. Izumiya, H. Ishakawa, and M. Mashita, J. Cryst. Growth **145**, 153 (1994).
[15] M. Mashita, H. Ishikawa, T. Izumiya, and Y. Someya Hiraoka, Jpn. J. Appl. Phys. **36**, 4230 (1997).
[16] W. Stolz, J. Cryst. Growth **209**, 272 (2000).
[17] S. Minagawa and M. Kondow, Electron. Lett. **25**, 758 (1989).
[18] H. Sai, H. Fujikura, and H. Hasegawa, Jpn. J. Appl. Phys. **38**, 151 (1999).
[19] S. F. Yoon, K. Y. Mah, and H. Q. Zheng, J. Appl. Phys. **85**, 7374 (1999).
[20] M. C. Wu, Y. K. Su, and C. Y. Chang, and K. Y. Cheng, J. Appl. Phys. **58**, 4317 (1985).
[21] Y. Ishitani, E. Nomoto, T. Tanaka, and S. Minagawa, J. Appl. Phys. **81**, 1763 (1997).
[22] U. Dörr, W. Schwarz, A. Wörner, R. Westphäling, A. Dinger, H. Kalt, D. J. Mowbray, M. Hopkinson, and W. Langbein, J. Appl. Phys. **83**, 2241 (1998).
[23] M. Kondow, S. Minagawa, and S. Satoh, Appl. Phys. Lett. **51**, 2001 (1987).
[24] J. S. Nelson, E. D. Jones, S. M. Myers, D. M. Follstaedt, H. P. Hjalmarson, J. E. Schirber, R. P. Schneider, J. E. Fouquet, V. M. Robbins, and K. W. Carey, Phys. Rev. B **53**, 15893 (1996).