Short-wavelength photoluminescence and electroluminescence in Ga(Al)P/GaP staggered type II quantum wells

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Photoluminescence spectra of tailored Ga(A1)P/GaP quantum well heterostructures exhibit strong short-wavelength peaks at 363, 560, and 600−700 nm. The peak at 560 nm seems to originate from a no-phonon transition. All the transitions are observed up to 200 K. Light emitting diodes made with the same heterostructure predominently emit 560 nm light (green) with a background of 700 nm (red) at room temperature under cw operation. © *1997 American Institute of Physics.* [S0003-6951(97)02948-3]

Various semiconductor materials and heterostructure systems, including the large-band gap nitrides, are being investigated for their suitability to realizing short-wavelength bright semiconductor light emitting diodes (LEDs) for displays and optical memories. In particular, reliable, room temperature light sources in the visible and ultraviolet regions of the spectrum are of great interest. Ordered and disordered GaP/Ga(Al)P superlattices have demonstrated visible luminescence which has been attributed to zone folding, band mixing, and the presence of localized and interface states.[1–5] More recently, strong luminescence, which is also more resistant to thermal quenching, has been observed in staggered type II GaP/AlP quantum well structures.[6] A sharp no-phonon peak observed in the photoluminescence (PL) spectra of these heterostructures is believed to originate from considerable overlap of the carrier wave functions and Γ–X bandmixing. We have investigated the PL spectra of band gap engineered $Ga_{0.6}Al_{0.4}P$/GaP quantum well heterostructures. In addition to the sharp no-phonon transition in the green, we observe a dominant broad emission in the ultraviolet (UV) region of the spectrum. Preliminary LEDs made with similar heterostructures exhibit significant green emission at room temperature.

The experimental samples were grown by atmospheric pressure metalorganic vapor phase epitaxy (MOVPE) on n^+ (Si-doped) and p^+ (Zn-doped) (100) GaP substrates misoriented 10° towards (110). One of the heterostructures for PL measurements is shown in Fig. 1(a), together with the schematic of the band diagram. The band lineups are calculated by linear interpolation from the known band gaps of 2.35 and 2.51 eV for GaP[7] and AlP,[8] respectively, and a reported valence band offset of 0.43[9] in the GaP/AlP type II heterostructure. The active region is repeated five times in both, to increase the luminescent efficiency. All the epitaxial layers in the PL samples are undoped. Variable temperature PL measurements were done using a quadrupled yttrium aluminum garnet (YAG) laser at 266 nm with an incident power of 5 mW (80 μm spot size), a 0.25 m scanning spectrometer, an air-cooled photomultiplier tube (PMT) sensitive to short wavelengths, and lock-in amplification. The resolution of the measurement is estimated to be 8 Å.

Low temperature (23 K) PL spectra from the sample shown in Fig. 1(a) are shown in Fig. 2. We have made PL measurements on several other heterostructures in which the thicknesses of the AlP, $Ga_{0.4}Al_{0.6}P$, and $Ga_{0.7}Al_{0.3}P$ layers have been varied. The peaks in the PL spectra shift in wavelength, but the general nature of the spectra remain the same. Before we try to interpret the origin of the various peaks, it is important to realize that these samples are not ordered or disordered superlattices, and therefore the observed PL does not result from zone-folding effects or other localized or interface states in such superlattices.[10] The sharp transition (labeled 2) in the spectra is the no-phonon transition which has also been observed and characterized by Issiki *et al.*[6] It results from a considerably large overlap of the electron and hole wave functions in these structures (close to a type I quantum well, as calculated by Issiki *et al.*) and large $\Gamma-X$

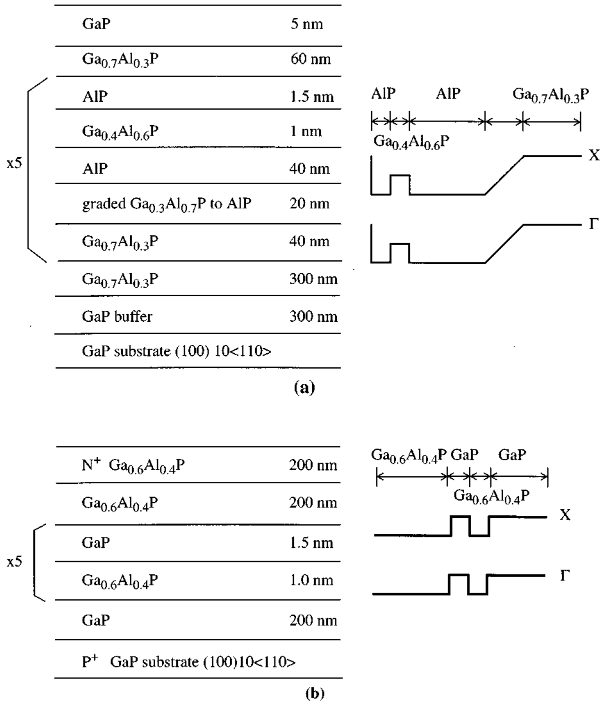

FIG. 1. Ga(Al)P/GaP heterostructures grown by MOVPE for (a) photoluminescence and (b) electroluminescence studies. Schematics of the band lineups are shown alongside.

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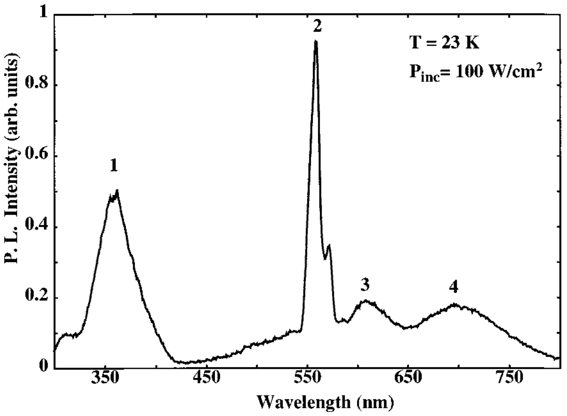

FIG. 2. Low temperature photoluminescence spectra measured for the sample shown in Fig. 1(a).

mixing due to breakdown of translational symmetry. The emission is essentially in the green region of the spectrum. The weaker peaks labeled 3 and 4 are consistently present, independent of the thickness and composition of the layers. At this point we conclude that they originate either from impurities in the substrate or from ubiquitous impurities in the wells or interface regions. As will be evident later, they contribute significantly to the output of electroluminescent devices.

The origin of the ultraviolet emission (peak 1, λ~363 nm), being observed for the first time, is not well understood since the higher lying conduction band structure, the effective masses, and band offsets are largely unknown. The center wavelength of the luminescence remains within 1 or 2 nm for all the structures studied. Thus, it is not clear how the composition of the wells plays a role in this luminescence. It was confirmed that peak 1 does not originate from intentional impurities or from the substrate itself. As with peak 2, the intensity of peak 1 was greater for thinner wells. In such epitaxial layers of a few monolayers, the interfacial bonds play a crucial role in determining the band structure. Several groups have done nonempirically based calculations of the band structure.[11–13] These methods will not accurately determine the band gap energies for the higher bands, but one study has shown the importance of the interface model on the transition strength.[14] The ultraviolet emission energy (3.42 eV) corresponds to the direct band gap of $Ga_{0.6}Al_{0.4}P$ and localized states at the Γ point are a possibility as the origin of the emission. This implies that the spontaneous emission lifetime for the ultraviolet transition must be relatively short compared to the $\Gamma-X$ scattering time.

Figure 3 shows the measured PL intensity of peaks 1 and 2 as function of temperature. The variations are fitted with the equation: $I=I_0/[1+A\ \exp(T/T_0)]$, where A is a constant and T_0 is a characteristic temperature, which is an approximate measure of the presence and density of localized states contributing to the PL.[15] From the fits shown in Fig. 3, the values of T_0 are derived to be 5.35 and 44.7 K for the 556 and 363 nm emissions, respectively. These values strongly suggest that peak 2 is not from a localized state, and, as mentioned earlier, it is believed to originate from a no-phonon transition. The large value of T_0 for the 363 nm transition (peak 1), on the other hand, suggests a high degree of localization, agreeing with our conclusion made above.

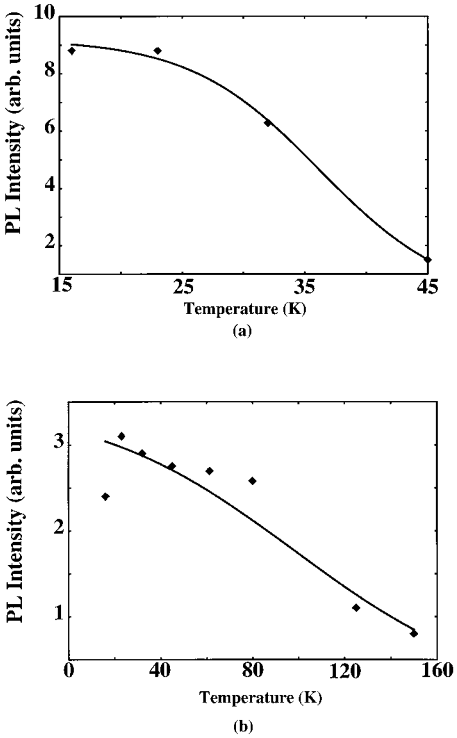

FIG. 3. Temperature dependence of the photoluminescence peak at (a) 556 nm and (b) 363 nm.

Electroluminescent (EL) diodes were made from the p-i-n structures shown in Fig. 1(b). Note that the active regions in the devices are different from those in Fig. 1(a). In other words, five periods of GaP and GaAlP quantum wells are stacked together, cladded by single thick barriers on either side. Photoluminescence measurements on a similar structure without the p^+ and n^+ layers yielded a spectrum identical to those in Fig. 2. It is therefore apparent that intrinsically there exists good electron and hole confinement and strong overlap of the wave functions in thin type II quantum wells. Two types of diodes were fabricated: mesa etched ones with a ring top contact for surface emission and cleaved bars (20 mm ×1 mm) with top and bottom contacts for edge emission (without any light confinement or guiding). The n and p contacts were made with Ni/Ge/Au/Ti/Au and Pd/Zn/Pd/Au, respectively. The diodes typically have a ~2 V forward turn-on and reverse voltages varying between 5 and 20 V. The measured room temperature EL spectrum under cw operation is shown in Fig. 4. Emission in the green and red are observed, which are also visible to the naked eye. These originate from peaks 2 and 4 in the PL spectra of Fig. 2. The relative magnitude of the red and green peaks is tunable with current injection. The output luminescence could not be extracted or collected efficiently since the device structure is not optimized. An output of 0.11 μW at 50 mA was measured from one facet of the edge emitting LED, remembering that the heterostructure is not designed as a waveguide. We believe that the actual light produced is at least 20 times more. Mesa diodes with top indium tin oxide (ITO) contacts

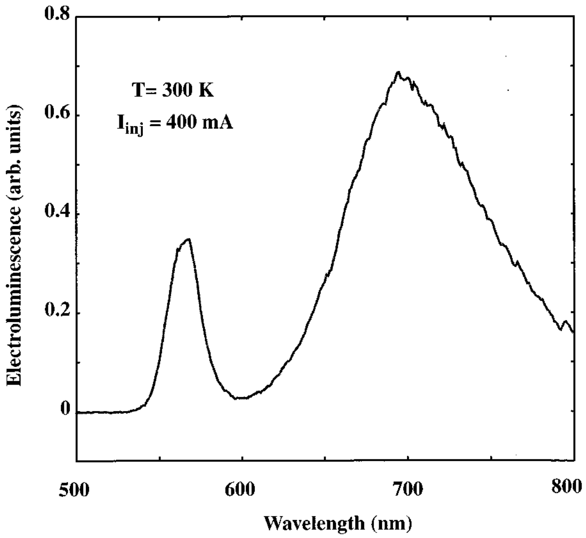

FIG. 4. Room temperature electroluminescence spectrum from LED made with heterostructure of Fig. 1(b) under cw operating conditions.

and edge emitting devices with waveguide heterostructures are being investigated.

The 363 nm emission was not observed in the EL spectra. This fact indirectly suggests that the luminescence may be related to the Γ point of GaAlP, in which case a higher band gap (Γ) contact layer, such as GaN, will have to be incorporated to inject electrons.

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