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Light-emitting diodes based on InP quantum dots in GaP

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Light emitting semiconductor devices are key components for information transmission, information storage, visible displays, and lighting. Most optical information transmission over glass fiber is in the infrared where direct-band gap semiconductors can provide high intensities. For emission in wavelengths consistent with human vision, early LEDs were only bright enough to be used as indicators or in the displays of early calculators and digital watches. Recently, the LEDs have been starting to appear in higher brightness applications; for example, the automotive industry has embarked on programs to replace all incandescent lamps in automobiles with LEDs. Another application for LEDs which is now becoming economically viable is in traffic signals, requiring highly visible red, yellow, and green emitters. Still another application for high-intensity green emission is in short-range data transmission using plastic optical fiber, where, unlike in glass fiber, the maximum transmission is in the green portion of the spectrum. The pre-condition for such useable LEDs is not only the wavelength of their emitted light, but also their light emitting efficiency or brightness. Today, commercialized red or green LEDs are based on GaP, which is an indirect band gap (2.26 eV) semiconductor. In order to achieve a useful efficiency, the GaP is doped with materials resulting in deep levels such as N or ZnO. Deep levels allow light emission by localizing the electronic wavefunction, thereby delocalizing it in k-space and introducing a non-zero momentum overlap of it with the hole wavefunction.

An alternative method to achieve efficient light emission from an indirect semiconductor such as GaP would be to introduce direct band-gap nanostructures such as quantum dots (QDs) into the GaP matrix. The spatial confinement of such QDs could also allow emission at much shorter wavelengths than would normally occur in the bulk form of the direct band-gap material. For example, the use of InAs QDs in a GaAs matrix for lasers is already well developed [1]. The realization of direct band-gap light emission is potentially of great importance because it could allow high efficiency light emission from within a GaP matrix and on a GaP substrate, taking advantage of the well-developed GaP-based light-emitting diode (LED) technology. Furthermore, using the transparent GaP rather than GaAs as substrate allows easier extraction of the emitted light for vertical structures such as super-luminescent LEDs or vertical cavity lasers.

Although InAs is also a candidate for direct band-gap QDs in GaP [2], for shorter wavelength emission InP is a more obvious candidate. We have recently described the formation of InP QDs using gas-source molecular beam epitaxy (GSMBE) [3]; in contrast with other reports, however, we are able to achieve intense optical emission from the GSMBE-prepared InP QDs [4].

Apparently, efficient recombination is only possible in relatively small InP QDs. InP deposition using a relatively low PH_3 flux of about 1 sccm (standard cubic centimeter per minute), results in InP islands with quite large lateral sizes; AFM measurements show average lateral sizes of 100 to 130 nm as the InP coverage is increased from 2 to 6 ML. The dot density changes in the range of 2–6×10^8 cm^{-2} and the average height of the dots is about 18–20 nm and nearly independent of InP coverage. These large dots form under low PH_3 flux even at deposition rates as low as 0.08 ML/s and a substrate temperature of 450°C. Preference for cluster nucleation may be here either because of reduction of the surface energy (Oswald ripening) or because of already existing dots. Furthermore, the formation of the large InP/GaP QDs compared to other highly lattice-mismatched III-V QDs may be explained by the large elastic constants in bulk InP. Higher PH_3 flux during InP deposition leads, however, to smaller islands. AFM measurements show for islands grown at 2 sccm (high flux) average lateral sizes of 15 to 50 nm as the InP coverage is increased from 2 to 5 ML. The dot density changes in the range of 2–20×10^9 cm^{-2} and the height of the dots is between 3 and 5 nm. Figure 1 shows AFM images from two samples containing 3 ML InP grown at a substrate temperature of 490°C under different PH_3 flux: 1 sccm (low flux) and 2 sccm (high flux). The dots grown under high-PH_3 flux are significantly smaller than those grown under the low-PH_3 flux condition because the higher PH_3 flux leads to a higher phosphorus surface density and lower In surface mobility. Besides the structural differences between the InP QDs grown under differing PH_3 fluxes, we obtain photoluminescence only from the smaller QDs grown under higher PH_3 flux. In our experiments, the lateral cut-off size for obtaining optical emission is about 50 nm, perhaps due to non-radiative recombination centers in the dots.

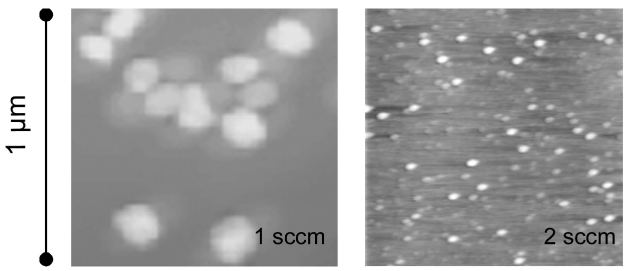

FIG. 1: AFM micrograph of two samples containing 3 ML InP grown under low PH_3 flux (1 sccm) and high PH_3 flux (2 sccm). Size of images are $1\times1\,\mu m^2$.

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Just because bulk InP is a direct band-gap semiconductor does not mean, however, that InP QDs in a GaP matrix will be direct. The strain and quantum confinement could lead to two of the X valleys in the InP lying below the Γ valley. Furthermore, depending on the band alignment between the GaP and InP, the X valleys in the GaP could be lower in energy than the InP Γ valley, again preventing direct band-gap recombination. These issues have been addressed in Ref. [5]. In this study, both photoluminescence (PL) as function of pressure as well as time-resolved PL indicate that at normal pressures, the recombination is, indeed, direct band-gap and type I. The conduction band discontinuity between the X valleys in the GaP and the Γ valley in the strained InP is found to be about 30 meV. Furthermore, the lower X valleys in the strained InP lie about 20 meV higher in energy than the Γ valley.

For the realization of InP/GaP QD LEDs, the small sized InP QDs are grown within a GaP p-i-n diode structure using a Riber 32P GSMBE system. First, a 200-nm Si-doped GaP buffer layer (n$\approx 5 \times 10^{17}$cm^{-3}) is grown. Between 3 and 5 monolayers (ML) of InP are deposited at 510°C at a rate 0.27 μm/h. After the InP deposition, the dots are capped by 3 nm GaP. This procedure is repeated three times. After this undoped region containing the QDs, 700 nm of Be-doped GaP (p$\approx 5 \times 10^{17}$cm^{-3}) is grown and finally capped with 10 nm Be-doped GaP (p$\approx 1 \times 10^{19}$cm^{-3}). The growth process is monitored using reflection high-energy electron-diffraction (RHEED); during GaP growth, the surface shows a (2×4)-reconstruction. At the beginning of InP-growth, the RHEED-pattern appears streaky, indicating two-dimensional growth. After deposition of about 2 ML InP, however, the large lattice mismatch between InP and GaP of about 7.7% results in the formation of Stranski-Krastanow InP QDs and RHEED-pattern gradually becomes spotty and less intense. LEDs with top ring contacts and diameter of 230 μm are then fabricated for EL measurements.

Similar to what we found using photoluminescence, both the InP wetting layer and the InP QDs contribute to LED emission [4, 6] The light output from the InP/GaP QDs LEDs consists of two lines peaked in the green and red ranges. The sharp green line having 20 nm full width at half maximum (FWHM) peaks at about 550 nm and appears to result from carrier recombination in the strained InP wetting layer and perhaps in the surrounding GaP matrix. The red line at about 720 nm is attributed to electron-hole recombination in the quantum dots.

Emission is obtained from the LEDs to above room temperature, but decreases in intensity because of the relatively small barrier for the electrons to escape into the GaP. Figure 2 shows the temperature evolution of EL spectra with a constant injection current of 100 mA. As the temperature is increased from 70 to 300 K, the EL peak maximum shifts from 720 nm to 752 nm, and remains red. This red-shift follows the temperature dependence of the band gap of InP bulk with about 300 meV offset. We point out that the electroluminescence from QDs is observed up to room temperature and the EL intensity decreases by a factor of 60 as the temperature is raised from 70 K to room temperature. We anticipate that by using (Al,Ga)P barriers, we can decrease this temperature dependence.

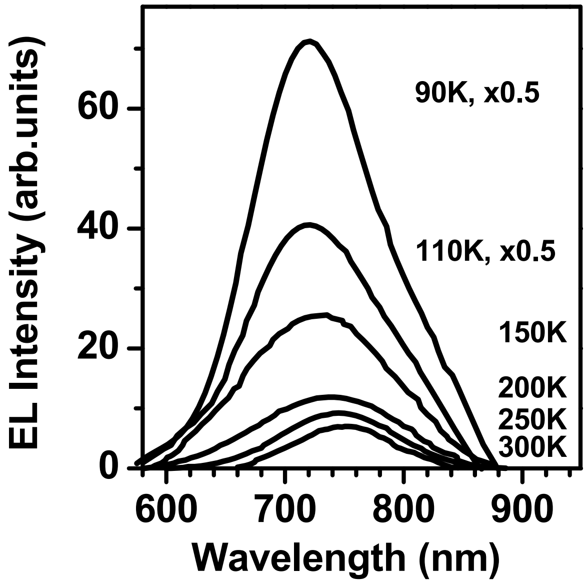

FIG. 2: Temperature evolution of the EL spectra under constant current of 100 mA.

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