

Optical characterization of disordered $\text{In}_x\text{Ga}_{1-x}\text{P}$ alloys

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We present results on the optical characterization of $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers grown by atomic layer molecular beam epitaxy on GaAs (001) substrates at a growth temperature of 420 °C. Our results show that the optical characteristics of these layers, which do not show ordering effects, are strongly dependent on surface stoichiometry during growth. In this way, we can obtain either highly homogeneous alloys with a predictable band-gap energy or layers with optical properties indicative of spatial localization effects, like an anomalous behavior of photoluminescence peak energy with temperature and a large shift between the emission energy and absorption edge. © 1998 American Institute of Physics. [S0003-6951(98)01920-2]

The $\text{In}_x\text{Ga}_{1-x}\text{P}$ alloy lattice matched to GaAs ($x = 0.48$) has enormous interest for its application in visible light emitters and as an alternative to AlGaAs in GaAs based devices. In particular, $\text{In}_x\text{Ga}_{1-x}\text{P}/\text{GaAs}$ based tandem solar cells have reached the highest efficiency achieved at present.¹

For device applications it is obviously necessary to know the band-gap energy of the alloy. However, it has been shown^{2,3} that formation during growth of ordered domains with CuPt structure decreases the effective band-gap energy and broadens the absorption edge.

This alloy exhibits other structural features, which are also growth dependent and are related to the existence of a miscibility gap in the range of growth temperatures used in some epitaxial techniques.⁴ This means that $\text{In}_x\text{Ga}_{1-x}\text{P}$ is thermodynamically unstable against separation into two phases of different compositions. In fact there is experimental evidence of some effects related to spinodal decomposition in layers grown by the usual nonequilibrium epitaxial techniques. For example, it is now well established that $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers show quasiperiodic variations in composition over ranges from a few nm to hundreds of nm.^{2,5-8} This modulated phase separation results in lattice strains which produce contrasts in transmission electron microscopy (TEM) images.⁹

CuPt-like ordering induces specific modifications in the band structure of the $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers, and the energy red-shift of the photoluminescence (PL) line is currently used as a measure of the degree of ordering.^{2,3} To our knowledge, the effect of compositional modulation, promoted by spinodal decomposition, on the optical properties of disordered layers have not been studied.

In this letter we present results on optical behavior of disordered $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers grown at low substrate temperature ($T_s \approx 420$ °C) by atomic layer molecular beam epitaxy (ALMBE). Structural characterization of the samples was made by high resolution x-ray diffraction (HRXRD) and Ra-

man spectroscopy, and results will be shown using PL and photoluminescence excitation (PLE).

According to our previous work,¹⁰ the $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers can show either a fine speckle structure with a size in the range 10–20 nm, or superposed to this, a long wavelength contrast (≈ 80 nm). These features have been related to alloy clustering and modulation composition effects, respectively.^{8,11}

From TEM studies, we know¹⁰ that these structural features strongly depend on growth conditions, in such a way that layers grown under “InGa rich” conditions, with a 2×4 surface reconstruction during growth as observed by reflection high energy electron diffraction (RHEED), show strong dark and bright fringes with a period of about 80 nm while those grown under “P rich” conditions which present a 2×1 surface reconstruction, just develop a fine structure (10–20 nm). Transmission electron diffraction studies also demonstrated that $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers grown by ALMBE are random in nature, with no evidence of appearance of ordered domains.

In this work, 1000 nm thick $\text{In}_x\text{Ga}_{1-x}\text{P}$ ($x = 0.48$, nominally) samples have been grown on GaAs (001) substrates at a growth rate of 1 monolayer per second under P rich or InGa rich growth conditions. The P_2 beam was produced by a special phosphorous solid source with a fast acting valve and cracking section. The growth process was monitored *in situ* by RHEED and reflectivity difference techniques.¹⁰ It is indicated that changes of growth front stoichiometry, and consequently the characteristic size of modulation composition features, can easily be obtained just by changing the time duration of the P_2 pulses in every monolayer cycle during growth. The composition and strain of the layers were obtained measuring two (004) and two (115) reflections by HRXRD. The simulation of the diffractograms gives, as the best fitting parameters, $x = 0.47$ and $x = 0.49$ for P rich and InGa rich samples, respectively.

Raman spectra of the $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers grown under InGa rich (continuous line) and P rich (dotted line) conditions are plotted in Fig. 1. Raman spectra have been taken in

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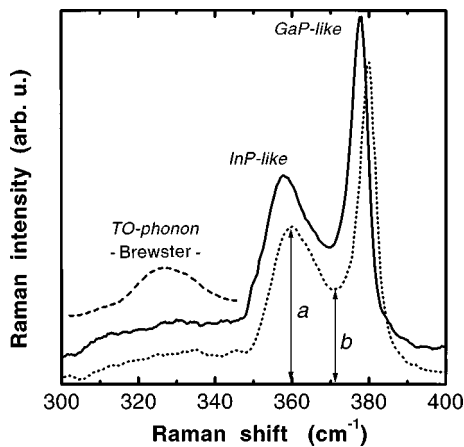


FIG. 1. Raman spectra of the $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers grown by ALMBE under InGa rich (continuous line) and P rich (dotted line) conditions. The dashed line corresponds to the TO-phonon resonance observed under Brewster angle configuration. The ratio b/a of the intensity at the valley between InP- and GaP-like LO phonons and the intensity of the InP-like phonon peak can be used as a measure of the degree of ordering of the alloy.

the backscattering geometry $\bar{Z}(X,X)Z$; other backscattering and near-Brewster angle geometries have also been used and only mention the better defined TO-phonon structure at about 327 cm^{-1} , when using Brewster angle configuration (dashed line in Fig. 1). The excitation wavelengths were the 514.5 and 488 nm lines of an Ar^+ laser for application of the Stokes/anti-Stokes method¹² in order to get a precision in the absolute Raman peak frequency better than 0.2 cm^{-1} . By using this method a small frequency shift of 2.2 (1.9) cm^{-1} is observed between the GaP (InP)-like LO-phonon peaks of the two layers. This frequency shift is related to the different value of x (0.47 and 0.49 for P rich and InGa rich layers, respectively), as determined by the HRXRD technique.

Raman spectroscopy can be used to quantify the degree of ordering and to determine the existence of domains with CuPt-like structure in these layers (see Refs. 13 and 14 and others therein). In the last case extra Raman peaks appear, even under usual backscattering geometries.^{13,14} The degree of ordering in the alloy is usually measured through the ratio b/a , where b is the intensity at the valley between InP- and GaP-like LO phonons and a the intensity of the InP-like LO phonon (see Fig. 1). A value around 0.6 can be considered as representative of a completely disordered alloy.¹³ Raman spectra measured in our layers (continuous and dotted line in Fig. 1) do not present other peaks than the typical ones in disordered $\text{In}_x\text{Ga}_{1-x}\text{P}$ alloys and a b/a value as high as 0.58 is obtained, practically the same value to that corresponding to completely disordered layers. Therefore, we can conclude that ordering effects are completely absent in our samples grown by the ALMBE method, as was expected from our previous TEM results.¹⁰

Figure 2 shows the PL spectra at $T=10\text{ K}$ of the same two $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers. The excitation source was the 514.5 nm line of an Ar^+ laser. A linewidth of about 10 meV measured for the P rich sample ($x=0.47$) indicates that the $\text{In}_x\text{Ga}_{1-x}\text{P}$ growth by ALMBE at low substrate temperature is a suitable growth technique for this material. On the contrary, the PL line observed in the InGa rich ($x=0.49$) sample is broader (35 meV) and redshifted about 60 meV with respect to that of the P rich. The different average composition

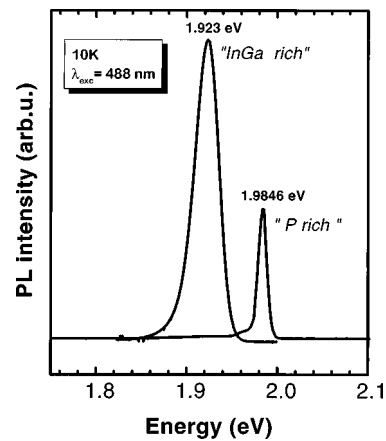


FIG. 2. Photoluminescence spectra taken at $T=10\text{ K}$ of 1000-nm-thick $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers grown by ALMBE on GaAs(001) under P rich ($x=0.47$) and InGa rich ($x=0.49$) growth conditions.

cannot explain a redshift larger than 20 meV, and consequently the PL peak energy is about 40 meV below the expected value for such a disordered alloy.

We have also carried out PL excitation around the alloy absorption edge at 4 K. Presently the setup is based on a 1/4 m double monochromator to obtain single wavelengths from a 1000 W Xe lamp. The spot size was larger and the incident power lower than in the case of PL spectra shown in Fig. 2. PL (continuous line) and PLE (dotted line) spectra taken with this new setup at $T=4\text{ K}$ from P rich and InGa rich samples are plotted in Fig. 3. The PL line recorded for the InGa rich sample is very similar (linewidth and peak energy) to the previous one, but the PL spectrum of the P rich sample now has two well resolved structures. The low energy line (23 meV redshifted) is thought to be related to an exciton bound to acceptor impurities, as it nearly disappears at a higher incident power (see Fig. 2). Their associated PLE spectra have the only resonance at 1.975 eV, the excitonic absorption of the $\text{In}_x\text{Ga}_{1-x}\text{P}$ alloy. The small Stokes shift (7 meV) between this resonance and the highest energy PL emission peak indicates that the dominant PL process is due to excitonic recombination.^{15,16} In fact, higher detection energies give the same PLE resonance at 1.975 eV and phonon resonances above the absorption edge, as occurs for good quality III-V semiconductors.

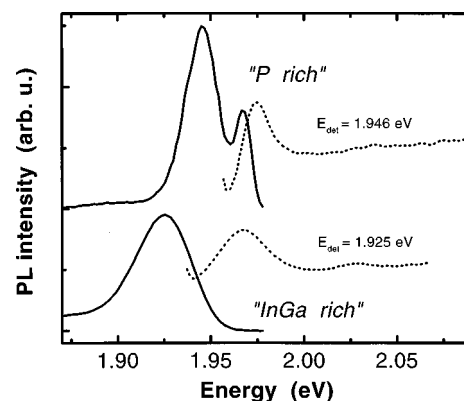


FIG. 3. Photoluminescence (continuous line) and excitation photoluminescence (dotted line) spectra taken at $T=4\text{ K}$ from P rich and InGa rich samples. The detection energy E_{det} is indicated in the plot.

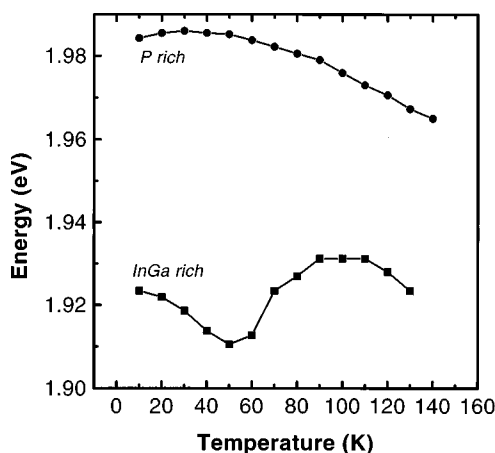


FIG. 4. Photoluminescence peak energy evolution with T from $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers grown by ALMBE on GaAs(001) under P rich ($x=0.47$) and InGa rich ($x=0.49$) growth conditions.

This is not the case for the InGa rich sample in which, apart from the slightly smaller energy of the exciton resonance in the PLE spectrum as expected from the difference in the average composition of the alloys, a broadband is observed both for the PL line and the exciton resonance in the PLE spectrum. We also observe a large energy difference between the PL and PLE peaks, as high as 43 meV, considering that this InGa rich layer does not exhibit CuPt-like ordering. This huge Stokes shift can only be due to strong spatial localization effects directly related to the presence of modulation composition features in $\text{In}_x\text{Ga}_{1-x}\text{P}$ samples grown under InGa rich conditions. Note that PL and PLE results shown in Figs. 2 and 3 correspond to different pieces of the studied samples, and so far, differences in energy between PL spectra shown in these figures can be explained by small differences in composition due to nonuniformities of our epitaxial setup. However this fact does not weaken our conclusion about the existence of localization effects.

The hypothesis given above, strong spatial localization effects in potential minima due to modulation composition features, used to explain the nature of the PL redshift in disordered InGa rich layers, also serves to explain the anomalous temperature dependence observed for the PL peak energy, as shown in Fig. 4. Whereas the PL peak energy measured in the P rich sample approximately follows the usual $\text{In}_x\text{Ga}_{1-x}\text{P}$ band-gap temperature dependence, the PL peak energy evolution in the InGa rich sample shows an abrupt redshift of PL peak energy below 100 K. This behavior could be explained considering that at low T the electron-hole pair has sufficient lifetime to drift into the lower band-gap areas with higher In content.

Similar behavior has also been observed in MOCVD grown $\text{In}_x\text{Ga}_{1-x}\text{P}$ alloys³ and it was ascribed to long range

ordering. Stokes shifts of 17 meV have been previously reported¹⁷ in disordered $\text{In}_x\text{Ga}_{1-x}\text{P}$ samples as due to alloy disorder phenomena. In this respect we want to notice that although the P rich samples show a fine speckle structure (TEM results) related to alloy clustering effects, we cannot observe any relevant Stokes shift, as corresponds to highly homogeneous alloys. This implies, in turn, that we are able to grow $\text{In}_x\text{Ga}_{1-x}\text{P}$ alloys with a strict control of band gap energy by choosing appropriate ALMBE growth conditions. On the other hand, samples grown under InGa rich conditions show Stokes shifts as large as 43 meV, which to our knowledge is the highest value reported in the literature for disordered $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers.

In summary, we observe that structural properties of $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers, which can be controlled during ALMBE epitaxial process by correctly choosing the growth conditions, are determinant for their optical properties. In this way, by changing the growth front stoichiometry we are able to obtain either highly homogeneous disordered $\text{In}_x\text{Ga}_{1-x}\text{P}$ alloys with accurate control of its band-gap energy, or inhomogeneous disordered $\text{In}_x\text{Ga}_{1-x}\text{P}$ layers which show clear localization effects related to the presence of modulation composition features. More experimental work is needed in order to take advantage of the localization effects produced by self-organized modulation composition structures.

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