

InGaP Layers Grown on Different GaAs Surfaces for High Efficiency Solar Cells

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ABSTRACT

InGaP layers grown on (111)Ga and (111)As GaAs substrate faces are investigated by microRaman spectroscopy, microphotoluminescence and cathodoluminescence. The growth on these polar faces benefits disorder with respect to the layers grown on (001) faces. It is shown that both (111)Ga and (111)As faces result in disordered InGaP layers. While the layers grown on (111)As faces present inhomogeneous compositions, the layers grown on (111)Ga faces present homogeneous compositions close to lattice matching and are almost disordered.

INTRODUCTION

Nowadays, there is a renewed interest on high efficiency solar cells, based on multi-junction structures of III-V compounds [1]. The ternary alloy InGaP is an essential material for multijunction cells. InGaP lattice matched to GaAs presents very interesting properties, as its direct bandgap of 1.9 eV. On the other hand, it presents some advantages respect to AlGaAs, as the absence of DX centers - which are responsible for a drastic reduction of the free carrier concentration in AlGaAs [2] -, larger band gap, and a more favourable band gap alignment with GaAs. It has been suggested that it might be useful for solar cells to make use of the growth on (111) GaAs faces under mismatched conditions, where large internal electric fields are generated by the off-diagonal strain [3]. In fact, the electronic band structure of QWs on (111) faces is substantially modified. The piezoelectric fields could allow for a better extraction of minority carriers and for a larger absorption coefficient [4]. Also, one might expect suppression of long range order, which is responsible for the band gap shrinkage and the change of the band alignment between InGaP and GaAs [5]; the presence of order has adverse consequences for the device performance. The growth modes on (111) faces are different from those on (001) faces, because of the different dangling bonds exposed and the different surface reconstructions. The optimization of the InGaP layers grown on (111) faces could provide a useful route to achieve better photovoltaic devices. This optimization demands a significant characterization effort, aiming to study the main structural and optical properties of the InGaP layers grown on (111) faces. This characterization needs to address problems as the control of the composition (short range order), spontaneous ordering (long range order), and the presence of defects. We explore here the preliminary growth by metal-organic chemical vapour deposition (MOCVD) of InGaP layers on (111)Ga and (111)As - GaAs substrates, and compare the results with the layers grown in the same conditions on (001) GaAs substrates.

Changes in the growth rate and composition are expected depending on the surface orientation used, because of the differences on the surface diffusion and sticking of the constituent atoms on the different surfaces. In order to control these changes, as well as the presence of ordered domains, optical measurements, microRaman (μR), microphotoluminescence (μPL), and cathodoluminescence (CL) were carried out. In that way, the optical properties of the different layers have been studied. The problems of ordering, phase separation and homogeneity are addressed, showing that InGaP/(111)Ga - GaAs structures present interesting perspectives for growing homogeneous disordered InGaP material.

EXPERIMENT

The layers were grown at 600°C under a reduced pressure of 60 mbar using TMGa and TMIIn, arsine and phosphine as main reagents. The MOVCD apparatus is a horizontal shaped one. The heating system consisted of a battery of 6 IR lamps focused to a graphite susceptor. In order to study the relationship between polarity and growth conditions, three GaAs substrates, (001), (111)Ga, and (111)As were used to growing simultaneously InGaP layers, with the lattice matched composition ($\text{In}_{0.49}\text{Ga}_{0.51}\text{P}$). Three different flows of phosphine, namely 290, 320 and 350 cm^3/min were used, keeping all other growth conditions unchanged, in order to study the effect of the V/III ratio on the layer properties. The growth on (111) faces, either Ga or As terminated, drastically changes the reagent adsorption and surface reaction mechanisms, which affects the growth rates and the distribution of the atomic species; therefore, changes in the layer composition and the growth rate might take place.

μPL measurements were carried out at room temperature exciting with an Ar^+ laser (514.5 nm), in a Labram UV-HR800 spectrometer (Jobin Yvon). The Raman spectra were measured in the same apparatus; therefore the μR and μPL data are fully comparable, since they were acquired in the same points of the samples.

CL measurements were carried out with a Xiclone –CL sytem from Gatan. The measurements were carried out at 80 K. The samples grown on (111) facets gave a much poorer CL signal than the samples grown on the (001) facet.

RESULTS AND DISCUSSION

The Raman spectrum of InGaP presents a two-mode behaviour [6]. It consists of a LO phonon mode (henceforth labelled LO_1) (GaP like) peaking at 381 cm^{-1} for GaAs lattice matched InGaP; a TO phonon mode (InP-like, TO_2) at 330 cm^{-1} , which is selection rule forbidden, although it is activated by alloy disorder; a phonon band appearing at 365 cm^{-1} has been associated with the InP-like LO phonon (LO_2) [7]. The frequencies and relative intensities of the modes are dependent on the composition, while the crystal orientation influences the relative intensity of the different phonon modes. Typical Raman spectra are shown in Fig.1a. One observes the LO_1 and LO_2 modes as the dominant ones in samples grown on (001) substrates. In samples grown on (111) substrates the TO_2 mode is strongly enhanced because of the crystal orientation. The Raman spectra of samples grown on (001) and (111)Ga substrates present a very good homogeneity over the full surface; however the Raman spectra of samples

grown on (111)As substrates are highly inhomogeneous over the wafer (the spectra at two different points are shown).

The Raman shift of the LO₁ phonon peak has been claimed not to be affected by the spontaneous order [8]; therefore, it can be used to give an estimation of the In_{1-x}Ga_xP composition according to the following relation:

$$\omega_{LO1} = 346.84 + 76.33x - 18.18x^2 \quad (1)$$

The data obtained for the different samples are reported in table I, where the corresponding composition is calculated with eq.(1). One observes that the samples grown on (001) substrates are very close to the lattice matched composition; some deviation and inhomogeneity were observed for the lowest phosphine flow. The samples grown on (111)Ga substrates are also close to lattice matching, but they present in average a slightly lower x. Finally, for samples grown on (111)As substrates the LO₁ phonon frequency presents a large dispersion, being generally shifted to the low frequencies, which accounts for In-rich compositions. In general, it seems that low phosphine flow benefits the incorporation of In, specially in the case of (111) faces. These data were checked over a large number of points, so they really reflect the properties of the different samples.

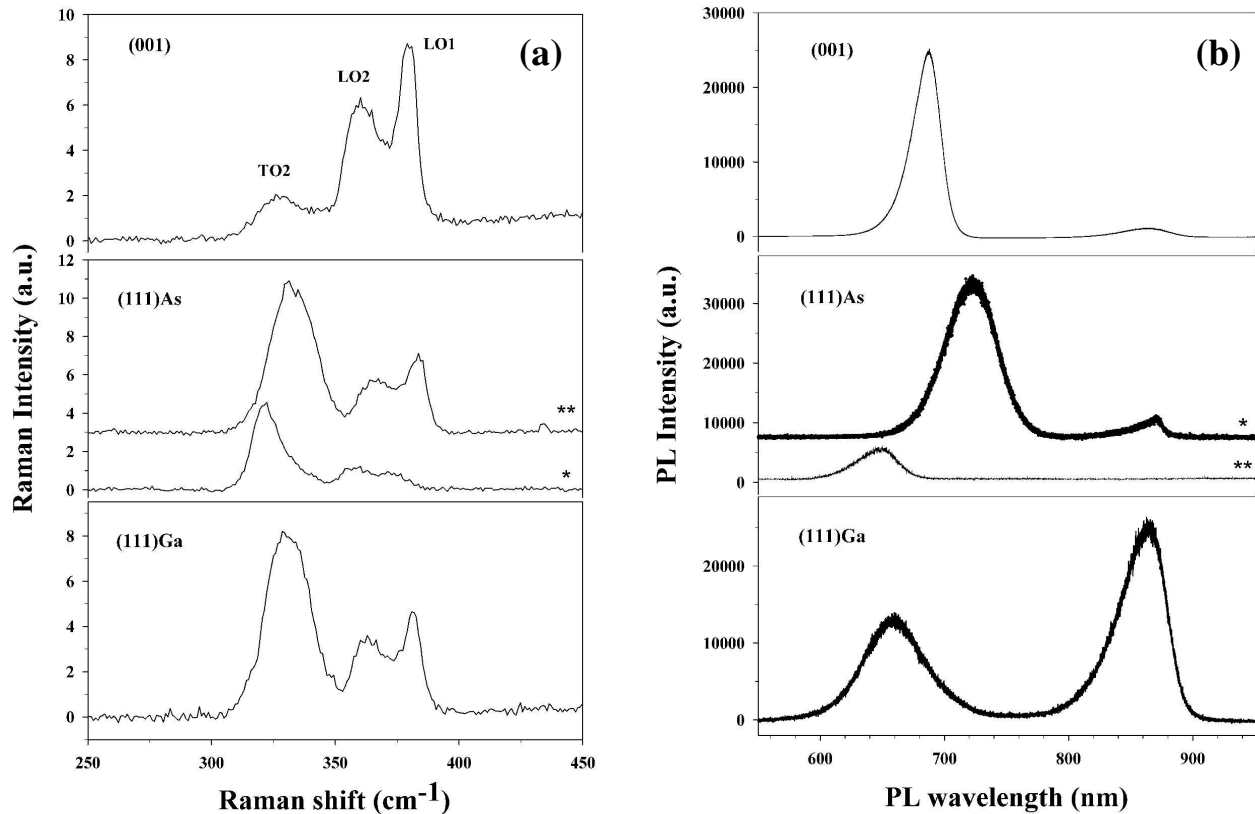


Figure 1. a) Raman and b) PL spectra of the studied samples. (Two points are shown for sample (111)As)

Table I. List of the studied samples, phosphine flux, LO₁ Raman peak position, estimated x from Raman shift, E_g values: E_g calc. (from the x values), E_g exp. (from the PL peak), and ΔE_g (=E_g calc.-E_g exp) (see text)

Face	Phosphine (cm ³ /min)	ω _{LO1} (cm ⁻¹)	x	E _g calc. (eV)	E _g exp. (eV)	ΔE _g (eV)
(001)	290	378.4–387.1	0.465–0.619	1.84–2.07	1.77–2.00	0.07
	320	381.2	0.513	1.91	1.80	0.11
	350	381.2	0.513	1.91	1.81	0.10
(111) As	290	364.3–383.5	0.243–0.553	1.57–1.97	1.59–1.94	-0.02–0.03
	320	373–383.4	0.376–0.551	1.72–1.97	1.71–1.97	0–0.01
	350	370.2–381.9	0.332–0.525	1.67–1.93	1.64–1.93	0–0.03
(111) Ga	290	379.6	0.485	1.87	1.83	0.04
	320	381.4	0.516	1.91	1.89	0.02
	350	379.5	0.484	1.87	1.87	0

The PL spectrum was acquired in the same points where the Raman spectra were taken. Typical PL spectra are shown in Fig.1b. For samples grown on (001) substrates one observes the InGaP emission, which the peak energy fluctuates around 690 nm (1.8 eV), without noticeable changes in the Raman spectra and the emission arising from the substrate. For samples grown on (111)Ga substrates the spectra are similar but the intensities are reversed, being the InGaP emission very weak compared to the (001) substrate, which is due to the much thinner InGaP layer on (111)Ga due to the lower growth rate on this face; the InGaP emission peaks around 667 nm (1.86 eV). Finally, the spectra of layers grown on (111)As substrates present the InGaP peak with a large spatial fluctuation, in agreement with the compositional changes reported from Raman data; on the other hand, some points exhibit a double peak, showing phase separation, with In-rich regions.

The E_g values estimated from the InGaP peak energy are reported in table I (E_g exp.). An estimation of the E_g values corresponding to the composition deduced from the LO₁ frequency was also done (E_g calc.). The band gap energy at room temperature of In_{1-x}Ga_xP ternary alloy free of strain and spontaneous order obeys to the following expression [9]:

$$E_g = 1.35 + 0.73x + 0.7x^2 \quad (2)$$

The values calculated are also reported in table I (E_g calc.), as well as the differences with the values obtained from the room temperature PL peak, ΔE_g.

One observes a very good matching between the two E_g values, experimental and calculated, for samples grown on (111)As substrates, which suggests the absence of order on these samples. The samples grown on the other face, (111)Ga, also give E_g values close to the value corresponding to their composition, which points to very low order degree. Finally the largest ΔE_g, and therefore the largest degree of order, are observed for the samples grown on (001) substrates.

CL images are shown in Fig.2 for the samples grown on (001) and (111)As faces. Fig.2a shows the peak wavelength distribution of the InGaP layer grown on the (001) face. One observes a cross hatched distribution, with an overall variation of the peak wavelength of ≈ 5 nm. The CL intensity of the InGaP emission also evidences the same cross hatched distribution, Fig.2b, which would be due to the charge confinement in the low energy domains. The images of the substrate emission also evidence the cross hatched distribution. The peak wavelength distribution of the substrate emission, Fig.2c, is very similar to the distribution of the peak wavelength of the InGaP layer. However, they are anticorrelated, and the overall wavelength variation is only ≈ 1 nm, which is much smaller than the peak wavelength fluctuation in the InGaP layer; this suggests that the peak wavelength shifts of the InGaP layer are due to ordering, rather than other effects as strain. The intensity of the substrate emission also follows the same pattern, Fig.2d, although the cross hatched structure is less defined. The distributions observed in the substrate are probably due to Si doping fluctuations. The n-type doping of the substrate is known to influence the degree of order [10]. These images evidence the relevant role of the substrate on the formation of the ordered domains.

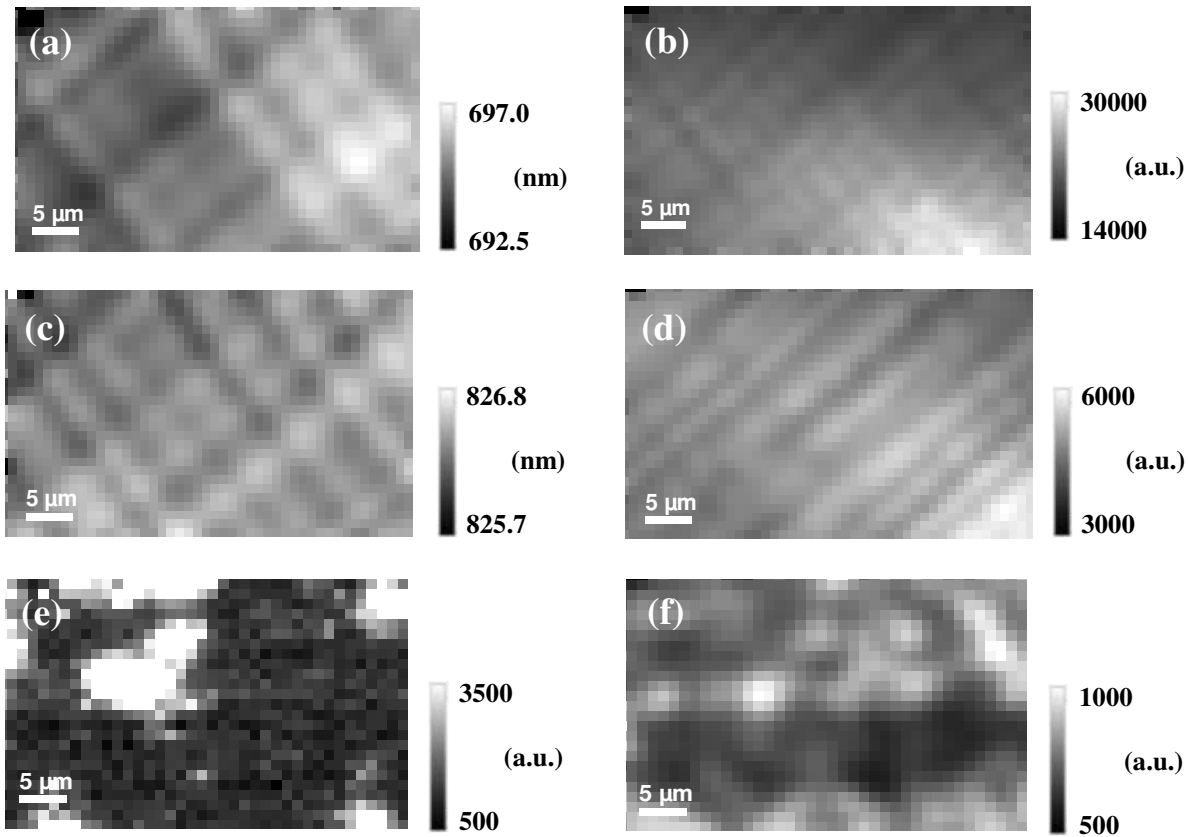


Fig.2. a) Peak wavelength distribution of the InGaP emission, b) monochromatic image at ~ 694 nm (corresponding to the InGaP emission), c) peak wavelength distribution of the substrate emission and d) monochromatic image at ~ 826 nm (corresponding to the GaAs emission) of a sample grown on a (001) face; e) monochromatic image at 656 nm (wavelength corresponding to nearly lattice matched composition) and f) monochromatic image at 710 nm (wavelength corresponding to In-rich regions), of a layer grown on a (111)As face.

The samples grown on (111)As substrates present islands with compositional variations, Fig. 2e) and f), which is in full agreement with the PL and Raman data that show a large compositional inhomogeneity of these samples. These islands can be propitiated by the very different diffusion lengths of In and Ga on this surface [11]. Finally, the samples grown on (111)Ga substrates appear more homogeneous than the other samples. However, the low growth rate difficult to obtain CL images because of the thin InGaP layers.

CONCLUSIONS

Ordering is substantially reduced in (111)As and (111)Ga faces; in particular, it is almost inexistent in (111)As faces, and very small in (111)Ga faces. Nevertheless, other problems have to be solved to grow high quality InGaP layers on the (111) faces, i.e. the control of the composition, which is particularly critical for samples grown on (111)As substrates, and the inhomogeneous growth. The layers grown on (111)Ga substrates present a low growth rate, and a tendency to be slightly In rich, in spite of the low degree of order and the good homogeneity. This preliminary research suggests that disordered InGaP can be grown on (111) GaAs substrates. Further growth runs modifying the growth parameters might presumably allow the improvement of the InGaP layers.

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REFERENCES

1. M. Yamaguchi, T. Takamoto, and K. Araki, *Solar Energy Materials & Solar Cells* 90, 3068 (2006).
2. P.M. Mooney, *J. Appl. Phys.* 67, R1 (1990).
3. D.L. Smith, *Sol. St. Commun.* 57, 919 (1986).
4. M. Hopkinson, J.P.R. David, E.A. Khoo, A.S. Pabla, J. Woodhead, and G.J. Rees, *J. Microelectron.* 26, 805 (1995).
5. Y.Zhang, A.Mascarenhas, and L.W. Wang, *Appl. Phys. Lett.* 80, 3111 (2002).
6. S. H. Wei and A. Zunger, *Phys. Rev. B* 49, 14337 (1994).
7. G. Lucovsky, M.H. Brodsky, M.F. Chen, J. Chicotka, and A.T. Ward, *Phys. Rev. B* 4, 1945 (1971).
8. M. Zachau, and W.T. Masselink, *Appl. Phys. Lett.* 60, 2098 (1992).
9. G. B. Stringfellow, *J. Appl. Phys.* 43, 3455 (1972).
10. S. Scardova, C. Pelosi, G. Attolini, B. Lo, O. Martínez, E. Martín, A. M. Ardila, and J. Jiménez, *Phys. Stat. Sol. (a)* 195, 50 (2003).
11. M.M.G. Bongers, P.L. Bastos, M.J. Anders, and L.J. Giling, *Journal of Crystal Growth* 171, 333 (1997).