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Photoreflectance study of partially relaxed epitaxial InGaAs on GaAs

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Room temperature photoreflectance (PR) spectroscopy and high resolution X-ray diffraction (HRXRD) have been used to investigate $In_xGa_{1-x}As$ layers grown compressively by MOVPE on GaAs substrates, with different composition and thickness. HRXRD reveals that all the samples are partially relaxed and In composition has been determined for each of the samples. The effects of residual strain on the optical response of the samples, namely interband transitions and the valence band splitting, were analyzed by fitting the standard line shape form to the PR data. The energies determined experimentally as a function of indium content were compared to those obtained in the framework of the elastic strain theory for pseudomorphic layers. This comparison allows us to estimate the extent of strain relaxation and to determine the residual strain values in the samples. Furthermore, we revealed that the measured residual strain ε_{res} follows $t^{-1/2}$ dependence on the epitaxial layers thickness t. This confirms the appropriateness of the nonequilibrium models (energy-balance models) for these structures.

Keywords: III-V semiconductors, PR spectroscopy, X-ray diffraction, strain relaxation, gallium indium arsenide.

1. Introduction

In recent years, a considerable interest has been devoted to the lattice mismatched $In_xGa_{1-x}As$/GaAs heterostructures from both technological and fundamental points of view. This follows from the fact that they find potential applications in manufacturing novel high-speed microelectronic and optoelectronic devices, because they offer nearly complete flexibility in tailoring their electronic and optical properties.

The epitaxial growth of these heterostructures is accompanied by elastic strain resulting from the differences in lattice parameters between the substrate and the epilayer.

The possibility of pseudomorphic growth of such structures, where the lattice mismatch is accommodated by the strain, enhanced the flexibility in tailoring their properties. The in-plane biaxial strain, arising at the interface with the substrate, considerably affects the electronic structure and optical response of the epitaxial layer, namely it shifts conduction and valence bands, removes the band degeneracy at critical points of the Brillouin zone, influences the electron (hole) effective mass and can also induce coupling between the neighbouring bands [1]. The achievement of the intended strain-dependent properties requires that the composition (x) and the thickness (t) of the epitaxial layer be carefully controlled. When the layer thickness exceeds a certain critical value (t_C) a stable elastic strain (ε) is relieved by the formation of misfit dislocations at the interface, usually accompanied by threading dislocations which can propagate up to the surface [2, 3]. This leads to a significant degradation of the layer quality that is detrimental to the performance and reliability of devices. The layers with thickness exceeding the critical value, *i.e.*, so-called partially relaxed layers, have still a residual strain ($\varepsilon_{\mathrm{res}}$) which depends on its composition and thickness. The study of fully strained as well as partially relaxed epitaxial layers is important for understanding the strain relaxation mechanism. The use of strain to tailor both the electronic and optical properties of materials requires the capability of modelling the process of strain relaxation and also the availability of modern investigation techniques.

In this paper, we report the investigations of the band gap changes, which are evoked by the presence of a residual strain in partially relaxed $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}/\mathrm{GaAs}$ heterostructures. Photoreflectance (PR) spectroscopy was employed to study the inter-band transitions. This technique due to its high sensitivity and the derivative nature of spectral line shapes [4] is an excellent tool to study the energy of the optical transitions. As was already shown, the PR can be exploited for measuring the residual strain in epitaxial layers, with the accuracy comparable to that of high resolution X-ray diffraction technique (HRXRD) [5–8]. PR is also a very useful tool for studying the critical thickness for lattice mismatched layers [9].

2. Experimental details

The $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ layers were grown on (001) GaAs substrates by metalorganic vapour phase epitaxy (MOVPE) at atmospheric pressure with AIX-200 R&D AIXTRON horizontal reactor. The standard organometallic group III precursors TMGa and TMIn as well as AsH_3 arsenic source reactant were used, respectively. The structure consists of a 500 nm thick GaAs buffer layer, doped with Si to net donor concentration $2\times10^{17}\ \mathrm{cm}^{-3}$, and of $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ epitaxial layer, with 5.5% (sample A), 7.7% (sample B), 8.6% (sample C) indium content x and different thickness t (210 nm, 250 nm and 280 nm, respectively), with the background net doping concentration of about $2\times10^{16}\ \mathrm{cm}^{-3}$. The In composition was determined by means of HRXRD

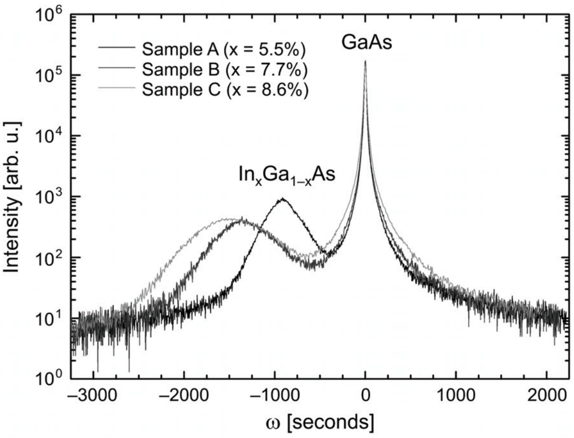

Fig. 1. X-ray rocking curves obtained using symmetrical (004) reflection for sample A (black line), sample B (gray line) and sample C (light gray line).

measurements performed by MRD Philips diffractometer, exploiting a four-crystal Bartels monochromator and CuKα1 radiation. The X-ray rocking curves of the (004) symmetrical reflection were then analyzed using dynamical diffraction analysis. The values of In content are presented in Fig. 1. All the epitaxial layers were grown at the same temperature equal to 670 °C, under compressive misfit strain conditions. The aim of the experiment was to obtain layers with thickness above a critical value and with a small lattice mismatch (less than 1.5%), *i.e.*, to obtain partially relaxed samples, for which strain relaxation occurs mainly by the formation of an orthogonal 2D network of 60° misfit dislocations at the epilayer-substrate interface [10]. The X-ray rocking curves, presented in Fig. 1, show very broad reflections from InGaAs epitaxial layers in comparison to those of the GaAs substrate and no interference fringes are visible. This indicates that all the samples are partially relaxed. Furthermore, by measuring two-dimensional (2D) reciprocal lattice maps (RLMs) for both asymmetrical (224) and symmetrical (004) Bragg reflections, we have revealed that the relaxation process is strongly anisotropic [11]. The observed anisotropic strain relaxation was in good accordance with the asymmetry in the formation of misfit dislocations at the epilayer-substrate interface, detected by transmission electron microscopy (TEM) [12]. A detailed analysis of the 2D RLMs, made it possible to calculate lattice parameters of the distorted unit cell, assuming the orthorhombic symmetry of all the $In_xGa_{1-x}As$ epitaxial layers [11]. The lattice mismatch is determined by the difference in lattice parameters between the layers and the substrate of about 0.39%, 0.55% and 0.62% for samples A, B and C, respectively.

The PR spectra were obtained using a conventional experimental set-up with a tungsten halogen lamp (150 W) as a probe light source, and a 632.8 nm laser was used as a modulation source. Phase sensitive detection of the PR signal was made using a lock-in amplifier and a silicon photodiode. Other relevant details of the PR set-up are described in [13].

3. Theoretical background

Pseudomorphic InGaAs epitaxial layers grown on (001)-oriented GaAs substrate are subjected to the in-plane biaxial strain, which causes a tetragonal compression of the layer [1]. For the critical point E_0, the strain can be decomposed into a hydrostatic component, which shifts the energy gap between the valence bands and the lowest conduction band, and the uniaxial strain component, which splits the heavy hole (HH) and the light hole (LH) valence bands. The resulting energy gaps between the conduction band and the split valence band can be expressed on the basis of the deformation potential theory by the following formulae [1]:

$$E_{\mathrm{HH}} = E_0 + \delta E_H - \frac{\delta E_S}{2} \tag{1a}$$

$$E_{\mathrm{LH}} = E_0 + \delta E_H + \frac{\delta E_S}{2} - \frac{(\delta E_S)^2}{2\varDelta_0} \tag{1b}$$

The values of δE_{H} and δE_S are given by the equations:

$$\delta E_H = 2a\left(1 - \frac{C_{12}}{C_{11}}\right)\varepsilon \tag{2a}$$

$$\delta E_S = 2b\left(1 + 2\frac{C_{12}}{C_{11}}\right)\varepsilon \tag{2b}$$

where a and b are the hydrostatic and shear deformation potentials, respectively, C_{11} and C_{12} are the elastic stiffness constants, $\varDelta_0$ is the spin-orbit splitting energy and ε is the biaxial strain in the plane of the interface given by $\varepsilon = [a_s - a_l(x)]/a_s$, where $a_l(x)$ and a_s are the lattice parameters of the $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ epilayer and the GaAs substrate, respectively. When the thickness of epilayer exceeds a certain critical value t_C the process of strain relaxation occurs. The partially relaxed $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ layer has still a residual strain $\varepsilon_{\mathrm{res}}$ which depends on its thickness t and composition x. Finally, the strain-dependent valence band splitting, as it can be measured from the optical spectra, is described by the equation:

$$\Delta E = E_{\mathrm{LH}} - E_{\mathrm{HH}} = \delta E_S - \frac{(\delta E_S)^2}{2\varDelta_0} \tag{3}$$

Table 1. Values of the deformation potentials C_{11} and C_{12}, and the elastic constants a and b from ref. [14], used in calculating strain-dependent changes in the band gap of partially relaxed $In_xGa_{1-x}As$.

Material	Lattice constant [Å]	C_{11} [GPa]	C_{12} [GPa]	a [eV]	b [eV]
InAs	6.0583	832.9	452.6	–5.08	–1.8
GaAs	5.65325	1221	566	–7.17	–2.0

The deformation potentials and the elastic constants, used in our calculations, are presented in Tab. 1 [14]. For the InGaAs ternary compound alloy, the corresponding material constants were obtained by a linear interpolation between relevant binary compounds.

4. Results and discussion

Figure 2 shows room temperature PR spectra of $In_xGa_{1-x}As$ layers with $x = 5.5\%$ (**a**), 7.7% (**b**) and 8.6% (**c**), respectively. The transition at 1.42 eV is related to the photon absorption in the GaAs buffer layer. The PR features below 1.42 eV correspond to the photon absorption in $In_xGa_{1-x}As$ epilayer. These features are composed of two resonances which are related to absorption between the HH and LH valence bands and

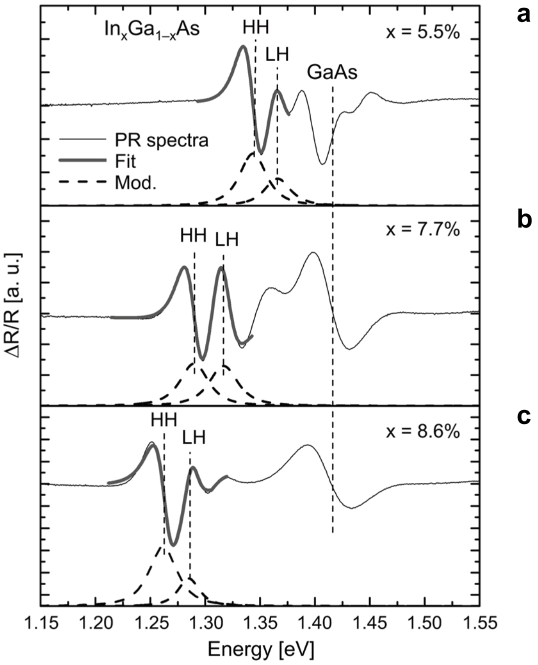

Fig. 2. Room temperature PR spectra of $In_xGa_{1-x}As/GaAs$ samples (thin solid lines) with $x = 5.5\%$ (**a**), $x = 7.7\%$ (**b**) and $x = 8.6\%$ (**c**). The bars mark the excitonic transition energies obtained from the best fittings (thick solid lines). Dashed lines represent the modulus of resonances of the individual lines.

the conduction band. The energy difference between these two resonances is related to the valence band splitting between LH and HH bands.

The PR spectra were analysed using the third-derivative Lorentzian line shape form in the low-field limit, characterizing electromodulated signals in bulk semiconductors, according to the well known Aspnes' relation [4, 15]:

$$\frac{\Delta R}{R} = \mathrm{Re}\left[Ae^{i\theta}\left(E - E_0 + i\Gamma\right)^{-m}\right] \tag{4}$$

where A and θ are the amplitude and the phase factor of the line shape, E is the energy of the probe beam, and E_0 and Γ are the critical point energy and its broadening parameter, respectively. The parameter m is the line shape factor, which depends on the type of a critical point (in our case for bulk-like transition $m = 2.5$). The best fit curves are shown by the solid lines in Fig. 2.

The energies of LH and HH transitions, determined from fitting the experimental data, are shown in Tab. 2. Since the energy splitting is directly evoked by a residual strain in the partially relaxed $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ epilayers, we can use it for estimating the extent of partial strain relaxation, which occurred in the samples. In order to determine the relaxation degree of the layers we have also calculated the valence band splitting energy for fully strained $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ layers with the same In content, lattice matched to GaAs. The theoretical splitting can be obtained from Eqs. (1)–(3), which take into account the effect of the strain in the layer. The lattice parameters of all the $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ epitaxial layers were calculated from the RLMs, revealed by HRXRD characterization [11].

Table 2. The values of the interband transition energies (E_{HH}, E_{LH}) and the valence band splitting obtained both from experimental studies (ΔE_{exp}) and theoretical calculations ($\Delta E_{\mathrm{theor}}$). Experimentally obtained indium content x and layer thickness t are also reported.

Sample	Indium content [%]	Layer thickness [nm]	Experiment			Theory
			E_{HH} [eV]	E_{LH} [eV]	ΔE_{exp} [eV]	$\Delta E_{\mathrm{theor}}$ [eV]
A	5.5	200	1.344	1.366	0.022	0.029
B	7.7	160	1.290	1.317	0.027	0.039
C	8.6	280	1.268	1.295	0.027	0.044

By taking into account the measured (ΔE_{exp}) and calculated ($\Delta E_{\mathrm{theor}}$) valence band splitting for the samples A, B and C (shown in Tab. 2), the percentage estimation of the extent of strain relaxation in epitaxial layer can be given by:

$$\eta = \frac{\Delta E_{\mathrm{theor}} - \Delta E_{\mathrm{exp}}}{\Delta E_{\mathrm{theor}}} \times 100\% \tag{5}$$

As was expected, the calculated valence band splitting $\Delta E_{\mathrm{theor}}$ for pseudomorphic layers increases monotonically with x while the measured valence band splitting ΔE_{exp}

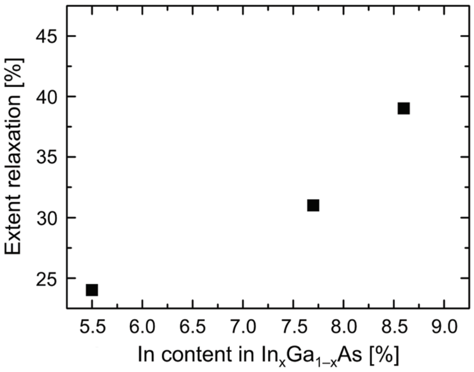

Fig. 3. PR-determined extent of strain relaxation in the partially relaxed In$_x$Ga$_{1-x}$As/GaAs heterostructures *vs*. In content.

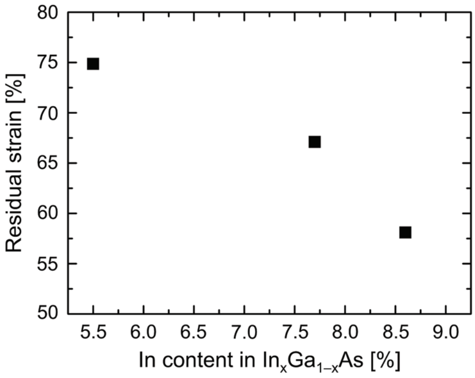

Fig. 4. PR-determined residual strain values of the partially relaxed In$_x$Ga$_{1-x}$As/GaAs heterostructures *vs*. In content.

is adequately lower but it does not change significantly. This is due to the fact that as a strain in the epitaxial layer starts to relax by means of plastic deformation of the crystal and generation of misfit dislocations, the valence band splitting decreases. The calculated percentage differences of HH-LH splitting between the fully strained and partially relaxed layers are 24%, 31% and 39% for samples A, B and C, respectively. Accordingly to Eq. (5), they can be treated as the percentage estimation of the extent of strain relaxation. In Fig. 3, the PR-determined extent of strain relaxation in all the samples investigated is shown as a function of In content.

Furthermore, in respect to Eq. (3), by taking the energy splitting ΔE_{exp} directly from PR resonance analysis (Eq. (4)), we were able (using Eq. (2b)) to calculate the residual strain values $\varepsilon_{\mathrm{res}}$ in our partially relaxed In$_x$Ga$_{1-x}$As epitaxial layers. For all the samples, the PR-determined residual strain values are shown in Fig. 4 as a function of In content. When the extent of a partial strain relaxation increases, the residual strain decreases inducing a smaller valence band splitting in every sample (compare ΔE_{exp} and $\Delta E_{\mathrm{theor}}$ in Tab. 2).

In Figure 5, the residual strain values $\varepsilon_{\mathrm{res}}$ for all the samples are presented as a function of the thickness *t*. The dotted and dashed lines correspond to two theoretical models representing the phenomenological predictions of the partial strain relaxation mechanisms in the layers. The former model, giving $\sim t^{-1}$ dependence of the strain

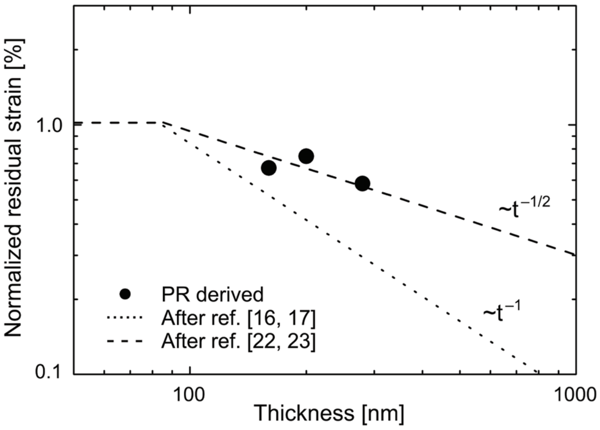

Fig. 5. PR-determined normalized residual strain value as a function of the thickness t of $In_xGa_{1-x}As$ epitaxial layers. The diagonal lines represent the layer thickness (t) dependence of the residual strain (ε_{res}) in the partial relaxation regime, predicted by equilibrium models ($\sim t^{-1}$ dependence – dotted line) [16, 17] or by nonequilibrium ones ($\sim t^{-1/2}$ dependence – dashed line) [22, 23]. The horizontal line corresponds to the pseudomorphic regime.

relaxation rate on the layer thickness [16, 17], belongs to the so-called equilibrium models on the basis of the continuum elasticity theory. This theory takes into account a thermodynamic equilibrium between the misfit dislocations network and the strained epitaxial layer [18–21]. It is expressed by minimizing the total energy of the system consisting of the elastic strain energy and the dislocation energy or by the equilibrium between the forces acting on threading dislocations, which elongate to form misfit dislocation segments at the interface. On the other hand, the model, yielding $\sim t^{-1/2}$ dependence of ε_{res} [22, 23], represents nonequilibrium models considering both the energy balance and nucleation mechanisms of new dislocations propagating as dissociated half loops (under the influence of the elastic stress field) from the surface towards the interface between the epitaxial layer and the substrate [23, 24]. The assumption relies on the increase of the half loop system energy during the expansion, until a larger loop is achieved and the energy reaches a maximum. Then the expansion continues reducing the total energy of the system [22].

As is shown in Fig. 5, the PR-derived experimental data match better the $\sim t^{-1/2}$ dependence of the residual strain in the partial relaxation regime than the $\sim t^{-1}$ one. A similar dependence has recently been observed in the mismatched systems of AlGaSb/GaAs [6] or in the case of metamorphic buffer layers in the InAs/InGaAs quantum dot (QD) structures [7, 8]. The results obtained in this paper indicate the validity of the latter, nonequilibrium model of strain relaxation. Most of the experimental observations of many epitaxial systems confirm that only the onset of the formation of misfit dislocations can be accurately predicted by the equilibrium theory while the strain release is limited by the nucleation of new dislocations [22]. Thus, measured critical layer thickness is as much as an order of magnitude larger than those foreseen by the equilibrium calculations. As a consequence, nonequilibrium models (energy balance and nucleation models) are more appropriate to describe the strain relaxation rate in lattice mismatch semiconductor heterostructures.

5. Conclusions

In conclusion, the partially relaxed $In_xGa_{1-x}As$ layers grown by MOVPE on GaAs substrates were investigated by HRXRD and PR spectroscopy. It has been shown that: *i*) the strain relaxation in $In_xGa_{1-x}As$ epilayers can be successfully determined from measurements of the valence band splitting by PR spectroscopy; *ii*) it has been observed that the investigated $In_xGa_{1-x}As$ layers with $x = 5.5\%$, 7.7% and 8.6% are relaxed in 24%, 31% and 39%, respectively; *iii*) the extent of strain relaxation of all the samples increases and the residual strain decreases as a function of the composition x and the layer thickness t; *iv*) the residual strain relaxation process of the heterostructures investigated follows the prediction of the nonequilibrium model, which yields $\sim t^{-1/2}$ dependence on the layer thickness.

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