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X-ray Study of Strain Relaxation in Heteroepitaxial AlGaAs Layers Annealed under High Hydrostatic Pressure

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The effect of treatment at up to 1270 K under hydrostatic argon pressure, up to 1.2 GPa, on strain relaxation of AlGaAs layers was investigated by X-ray diffraction and related methods. The 1.5 μm thick AlGaAs layers were grown by molecular beam epitaxy method on 001 oriented semi-insulating GaAs substrate at 950 K. An increase in intensity of X-ray diffuse scattering, originating from hydrostatic pressure-induced misfit dislocations, was observed for all treated samples. For the samples treated at 920 K during 1 h under 0.6 GPa, the diffuse scattering was confined to the [110] crystallographic direction perpendicular to the direction of dislocations. For the samples treated at 1.2 GPa at the same temperature and time conditions as for 0.6G Pa, a different behaviour is observed, namely the diffuse scattering extends along all azimuthal directions, indicating that dislocations are created in both [110] and [$\bar{1}$10] directions. The change of strain after the treatment was most pronounced for the samples treated at 1.2 GPa for 1 h at 920 K.

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1. Introduction

Low dimensional epitaxial structures based on III–V compound semiconductors are of high technological interest owing to a wide variety of applications including optical telecommunication and computing as well as quantum electronics. The lattice mismatch across the interface between the epitaxial layer and the substrate can be accommodated by uniform elastic strain until the critical layer thickness is reached. When the critical thickness is exceeded, the stresses favour creation of dislocations.

It is generally believed that misfit dislocations substantially degrade transport properties of semiconductors. Therefore, considerable research activity has been devoted to study the mechanism by which the strain relaxation occurs in heteroepitaxial systems. It is known that annealing of such systems at high hydrostatic pressure (HP) of ambient gas (HT–HP treatment) causes a decrease in defect density of the crystal [1]. An influence of the HT–HP treatment on the strain state of GaAs/Si, InAs/GaAs and InGaAs/InP structures has been reported earlier [2–4]. Such treatment results also in other effects at the layer/substrate interface. For example, the HT–HP treatment has been reported to affect the defect structure of the AlGaAs/GaAs heteroepitaxial samples [5]. For an $Al_{0.27}Ga_{0.73}As$ sample, the creation of dislocations aligned in the $[\bar{1}10]$ direction was observed after the HT–HP treatment for 1 h at 1.2 GPa at a temperature close to that of the layer growth [6].

Investigation of the influence of applied pressure, temperature, and treatment duration on the strain state of the AlGaAs/GaAs heteroepitaxial layers and on their defect structure was the main goal of our work. The study was focused on detection of the change of anisotropic distribution of defects created during the HT–HP treatment.

2. Experimental

The 1.5 μm thick AlGaAs layers of different Al contents were grown at $T = 950$ K by molecular beam epitaxy (MBE) on the (001) oriented semi-insulating GaAs substrates. The samples were HT–HP treated at up to 1270 K under argon pressure up to 1.2 GPa for 1–10 h. The HT–HP equipment was described elsewhere [7].

X-ray investigations were carried out using a MRD-PHILIPS diffractometer in the double and triple configurations. The measurements of the full width at half maximum (FWHM) of the rocking curve and reciprocal space mapping for symmetrical reflections were performed for the two sample positions, with the [110] and $[\bar{1}10]$ directions perpendicular to the diffraction plane. The in-plane crystallographic direction was determined from the shape of etch pits revealed by preferential chemical etching.

For the samples treated at 1.2 GPa at a temperature lower than that of layer growth (720 K), X-ray topographs were taken at the F1 station in HASYLAB using white synchrotron beam. X-ray patterns were recorded with the film perpendicular to the incident X-ray beam at a 10–30 cm distance.

The strain of the samples was calculated from the lattice parameters. The in-plane and out-of-plane lattice parameters of the layer material were measured before and after the treatment from the symmetrical 004, 006, and asymmetrical 335 and 224 reflections, by the method described in [8]. The relaxed lattice parameters, a_{relax}, were next calculated. The sample composition was determined by two methods: (i) from the relaxed lattice parameter assuming Vegard's rule and (ii) for untreated and treated during 1 h samples by secondary ions mass spectrometry (SIMS).

PL spectra were excited at 4.2 K with the 488 nm line of Ar laser. A CCD camera was used as a detection tool.

3. Results

The $Al_{0.4}Ga_{0.6}As$/GaAs and $Al_{0.7}Ga_{0.3}As$/GaAs structures (defined in Sec. 2) exhibited structural changes after the HT–HP treatment while no change was found after annealing under atmospheric pressure (10^5 Pa). The HT–HP treatment did not affect the concentration profiles of Al, As, and Ga (as determined by SIMS) in the studied layers. For the HT–HP treated $Al_{0.4}Ga_{0.6}As$/GaAs and $Al_{0.7}Ga_{0.3}As$/GaAs layers the influence of HT–HP treatment on their defect structure was similar, therefore the illustrating reciprocal space maps are included in this paper only for the representative $Al_{0.4}Ga_{0.6}As$/GaAs layer. The studied samples with treatment conditions are listed in Table I.

TABLE I

The treatment conditions for $Al_{0.4}Ga_{0.6}As$/GaAs (samples 1A–1F) and $Al_{0.7}Ga_{0.3}As$/GaAs (samples 2A–2F) layers.

Samples	Applied pressure [GPa]	Treatment temperature [K]	Treatment duration [h]
1A, 2A	–	–	–
1B, 2B	1.2	720	1
1C, 2C	1.2	920	1
1D, 2D	1.2	1070	1
1E, 2E	0.6	920	1
1F, 2F	1.2	920	10

A change of FWHM value was detected only for the samples 1B, 2B, 1C, and 2C (see Table II). FWHM did not depend on the layer orientation. An increase in

TABLE II

The values of FWHM for 004 reflection (L — layer, S — substrate) and of strain, ε, for $Al_{0.4}Ga_{0.6}As/GaAs$ and $Al_{0.7}Ga_{0.3}As/GaAs$ structures, as-grown and treated at 720 K and 920 K under 1.2 GPa for 1 h.

Sample and treatment	FWHM [arcs] 004 reflection				Strain, $\varepsilon \pm 2 \times 10^{-4}$	
	Initial		After HT–HP treatment		Initial	After HT–HP treatment
	S	L	S	L		
$Al_{0.4}Ga_{0.6}As/GaAs$						
920 K – 1.2 GPa – 1 h (1C)	17	19	19	33	-5.7×10^{-4}	-6.9×10^{-4}
920 K – 1.2 GPa – 10 h (1F)	17	19	17	23	-5.7×10^{-4}	-6.0×10^{-4}
720 K – 1.2 GPa – 1 h (1B)	17	19	17	23	-5.7×10^{-4}	-6.1×10^{-4}
$Al_{0.7}Ga_{0.3}As/GaAs$						
920 K – 1.2 GPa – 1 h (2C)	19	23	19	25	-1.05×10^{-3}	-1.13×10^{-3}
720 K – 1.2 GPa – 1 h (2B)	19	23	19	28	-1.05×10^{-3}	-1.10×10^{-3}

the out-of-plane lattice parameter and a decrease in the in-plane one were found for the 1C sample. This effect was less pronounced (within the error limit) for the samples 1B and 2B (see Table II).

In the case of AlGaAs/GaAs treated at a still higher temperature and pressure (sample D) as well as for the sample E and sample F, no change of lattice parameters was detected. In spite of the fact that no change of the lattice constant value was found for the sample D and sample F their PL spectra indicated a slight

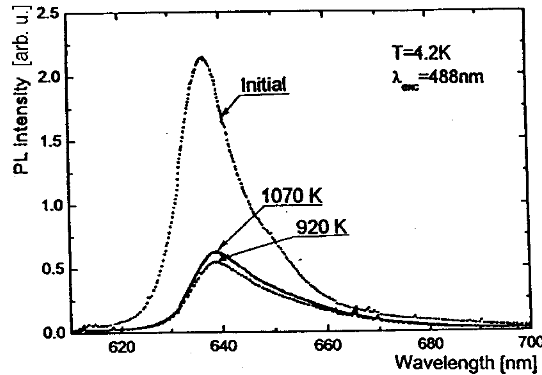

Fig. 1. PL spectra of $Al_{0.4}Ga_{0.6}As/GaAs$ samples, initial, and treated at 920 K and 1.2 GPa for 10 h, at 1070 K and 1.2 GPa for 1 h.

shift to higher wavelength (Fig. 1). It leads to a conclusion that a compressive strain decreased as a result of the treatment (the biaxial compressive strain causes an increase in the energy gap).

An increase in diffuse scattering after the treatment was observed at the reciprocal space maps. Diffuse scattering intensity depended on the pressure value, temperature, and treatment duration. The reciprocal space maps for the $Al_{0.4}Ga_{0.6}As/GaAs$ sample taken with the $[\bar{1}10]$ direction perpendicular to the diffraction plane are presented in Fig. 2. For the samples treated at 1.2 GPa for 1 h, the diffuse scattering intensity from the GaAs substrates increased with increasing treatment temperature. The diffuse scattering intensity from the layer of the sample 1B remained practically the same as that from the initial samples, but increased for the case of sample 1C. Also no creation of additional dislocation for the sample B treated was detected by X-ray synchrotron topography.

For the treatment temperature fixed at 920 K, the diffuse scattering intensity from the layer and substrate materials decreased with treatment time (from 1 h to 10 h) but increased with pressure (from 0.6 GPa to 1.2 GPa). In the case of treatment at 1070 K, the diffuse scattering from the layer material was of lower intensity than that from the samples treated at 920 K, but of higher intensity than that from the untreated samples. The diffuse scattering intensity, for 1D, 1E, and 1F samples was orientation-dependent (Fig. 3). The diffuse scattering intensity was higher when the diffraction plane was perpendicular to the $[\bar{1}10]$ direction.

4. Discussion

Additional strain created at HP results in the changed in-plane ($a_{\|}^{\mathrm{HP}}$) and relaxed ($a_{\mathrm{relax}}^{\mathrm{HP}}$) lattice parameters of the AlGaAs layer material. This change is described by the following formula:

$$a_{\|}^{\mathrm{HP}} = a_{\|}^{0} - \left(\frac{HP}{3B_{\mathrm{S}}}\right) a_{\|}^{0}, \tag{1}$$

$$a_{\mathrm{relax}}^{\mathrm{HP}} = a_{\mathrm{relax}}^{0} - \left(\frac{HP}{B_{\mathrm{L}}}\right) a_{\mathrm{relax}}^{0}, \tag{2}$$

where $a_{\|}^{0}$ and a_{relax}^{0} — the initial in-plane and relaxed lattice parameters of the AlGaAs layer material, HP is the applied pressure, and B_{S}, B_{L} are the bulk moduli of the substrate and layer materials, respectively.

At HT–HP the in-plane ($a_{\|}^{\mathrm{HT-HP}}$) and relaxed ($a_{\mathrm{relax}}^{\mathrm{HT-HP}}$) lattice parameters are described by the following formula:

$$a_{\|}^{\mathrm{HT-HP}} = a_{\|}^{\mathrm{HP}} + \Delta T \alpha_{\mathrm{S}} a_{\|}^{\mathrm{HP}}, \tag{3}$$

$$a_{\mathrm{relax}}^{\mathrm{HT-HP}} = a_{\mathrm{relax}}^{\mathrm{HP}} + \Delta T \alpha_{\mathrm{L}} a_{\|}^{\mathrm{HP}}, \tag{4}$$

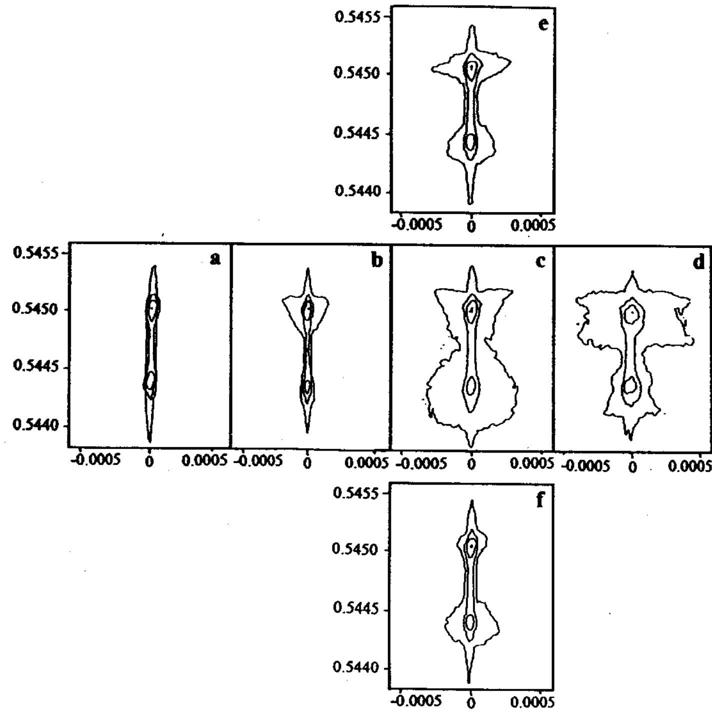

Fig. 2. 004 reciprocal space maps of the $Al_{0.4}Ga_{0.6}As/GaAs$ sample aligned with diffraction plane perpendicular to the $[\bar{1}10]$ direction; (a) untreated; (b) treated at 720 K and 1.2 GPa for 1 h; (c) treated at 920 K and 1.2 GPa for 1 h; (d) treated at 1070 K and 1.2 GPa for 1 h; (e) treated at 920 K and 0.6 GPa for 1 h; (f) treated at 920 K and 1.2 GPa for 10 h. The lower reciprocal lattice point on each map corresponds to the layer material and the higher one — to the substrate. The axes are marked in $\lambda/2d$ units. The intensity ratio of neighbouring contours is equal to 10.

where ΔT is an increase in temperature, and α_S, α_L are the thermal expansion coefficients of the substrate and layer materials, respectively.

The in-plane strain in the layer, $\varepsilon_{\|}$, is defined as

$$\varepsilon_{\|} = \frac{a_{\|} - a_{\mathrm{relax}}}{a_{\mathrm{relax}}}. \tag{5}$$

The sample strain during the HT–HP treatment can be estimated using the values of lattice parameters calculated from Eqs. (3) and (4). Compressibility (at 700 K – 1.2 GPa) of AlAs ($B_{\mathrm{AlAs}} = 83$ GPa) is almost the same as that of GaAs ($B_{\mathrm{GaAs}} = 81$ GPa). Due to specific values of thermal expansion coefficients ($\alpha_{\mathrm{AlAs}} = 5 \times 10^{-6}$ K^{-1}, $\alpha_{\mathrm{GaAs}} = 6.7 \times 10^{-6}$ K^{-1}) and of bulk modulus of the layer and substrate materials, the layer strain during the treatment is tensile (the bulk modulus and thermal expansion coefficient of AlGaAs layers were linearly interpolated).

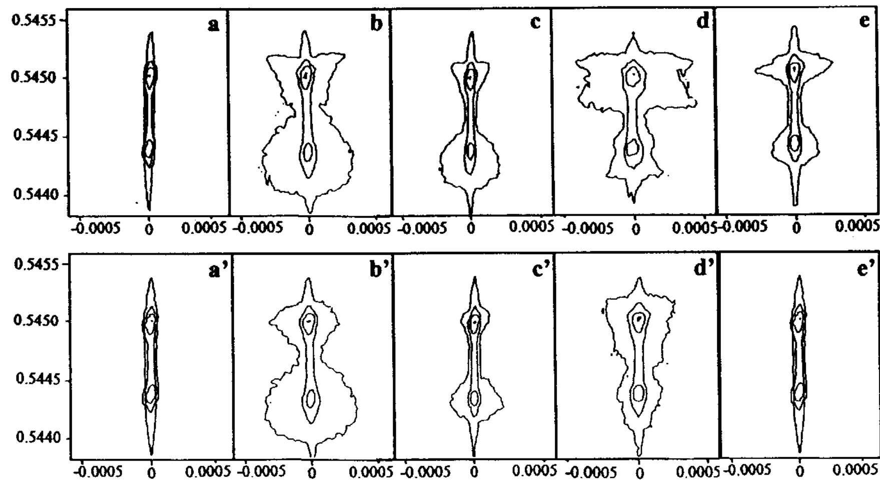

Fig. 3. 004 reciprocal space maps of the $Al_{0.4}Ga_{0.6}As/GaAs$ sample; (a, a') untreated; (b, b') treated at 920 K and 1.2 GPa for 1 h; (c, c') treated at 920 K and 1.2 GPa for 10 h; (d, d') treated at 1070 K and 1.2 GPa for 1 h, (e, e') treated at 920 K and 0.6 GPa for 1 h. The symbols a, b, c, d, e and a', b', c', d', e' correspond to the samples aligned with the diffraction plane perpendicular to the $[\bar{1}10]$ or [110] directions, respectively. The axes are marked in $\lambda/2d$ units. The intensity ratio of neighbouring contours is equal to 10.

The direction of the in-plane lattice-parameter change depends on the treatment temperature as shown in Fig. 4. At the first stage of the HT–HP treatment, pressure (HP) is increased while temperature remains unchanged. The change of the in-plane lattice parameter during that stage is marked by an arrow (transition from point 1 to point 2). In the next stage, temperature increases to the final value (HT) and the in-plane lattice parameter rises (transition from point 2 to 3) accordingly to Eq. (3).

Changes of the relaxed lattice parameter during the HT–HP treatment are depicted schematically as a transition between points A and C through the point B. When relaxation takes place at HT, the in-plane lattice parameter value is shifted to the relaxed one (transition from point 3 to 4). After release of HT–HP to ambient conditions (transition $4-5-6$), the in-plane lattice parameter, $a_{\|}^{\mathrm{end}}$, is smaller than that of the as-grown layer ($a_{\|}^{\mathrm{end}} < a_{\|}^{0}$). Below 900 K, the annealing is expected to cause an increase in the lattice parameter, but a decrease above 900 K (see Fig. 4). Indeed, a decrease in the in-plane lattice parameter is observed for samples treated during 1 h at 920 K (close to growth temperature), while an increase for the samples treated at the same temperature during 10 h and for samples treated at higher temperature (1070 K) is deduced from the lumincescent line shift. The in-plane lattice parameter changes are presented in Fig. 4 only schematically. Microscopic properties of solids and dislocation interaction are not taken into account in the above scheme.

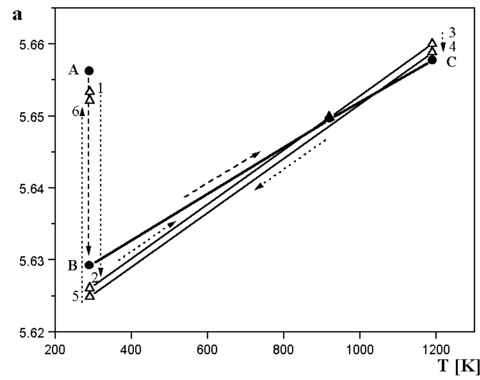

Fig. 4. Semi-schematic drawing of the changes of the in-plane and relaxed lattice parameters of the $Al_{0.4}Ga_{0.6}As$ layer grown on the GaAs substrate, during high temperature — high pressure (1.2 GPa) treatment ("•" — relaxed lattice parameter, "Δ" — in-plane lattice parameter).

Relaxation of the layer material ought to be concomitant both with the generation of dislocations and with the increased lattice mismatch at HT–HP, as compared to that during layer growth.

Generation of dislocations during the HT–HP treatment at a temperature close to that of layer growth was earlier observed on X-ray synchrotron topographs [6]. These dislocations are responsible for increased diffuse scattering observed around the reciprocal lattice point of the layers. For the lower temperature of treatment (720 K), the strain created at HT–HP was too small to produce additional dislocations. This justifies the lack of changes of defect structure on the X-ray synchrotron topographs and explains the diffuse scattering around the reciprocal lattice point of the layers remaining practically unchanged.

The mismatch, calculated from the material-parameter values, remained practically unchanged at 920/1070 K – 1.2 GPa. The calculated mismatch was 8×10^{-5} or 10×10^{-5}, in dependence on the thermal expansion coefficient value adapted for calculation. The latter can be assumed to be equal to 6.04×10^{-6} K^{-1} or 6.7×10^{-6} K^{-1} [9].

The explanation of the observed lattice parameter changes is not straightforward: strain relaxation demands accounting for the fact that both thermal expansion coefficient and bulk modulus are dependent on the sample defect structure and electron concentration [9] as well as on pressure value. The second effect, influencing the change of strain, can be connected with increased dislocation mobility at HT–HP conditions. This effect was observed for GaAs/Si structures [2]. Changes of elastic properties and/or of dislocation mobility under pressure can explain our observation that the treatment causes a detectable change in the strain state, although the difference between bulk modulus of the layer and substrate materials

is small. It means also that influence of the HT–HP treatment on defect structure of the layers depends mostly on the pressure and temperature values but much less on the layer composition.

The observed rocking-curve broadening in respect to the layer in the HP treated samples is attributed to the presence of threading dislocations as well as on other defects created during the treatment (a similar effect was reported earlier [5]). Density of threading dislocations is dependent on misfit dislocation density. The presence of misfit dislocations affects simultaneously the diffuse scattering intensity around the reciprocal space points (RSP) of the layer and substrate materials. It is known that for the heteroepitaxial samples with misfit dislocations oriented in one direction only, the diffuse scattering is confined to a crystallographic direction that is perpendicular to the direction of dislocations. For the samples with misfit dislocations oriented in the both [110] and [$\bar{1}$10] directions, the X-ray diffuse scattering extends along all azimuthal directions. Therefore, different dislocations densities for the [110] and [$\bar{1}$10] directions cause a dependence of the diffuse scattering intensity on the azimuthal orientation of the sample. It means that diffuse scattering depends on orientation. An increase in the diffuse scattering intensity around the RSP of the substrate or layer materials is related to generation of additional defects in the substrate or layer materials. During the treatment at lower pressure (0.6 GPa) the dislocations in the [$\bar{1}$10] direction were created, as it follows from reciprocal space map, but the change of strain was too small to be experimentally detected. The misfit dislocations network was generated during the treatment at some pressure between 0.6 and 1.2 GPa. This effect was more pronounced for the treatment temperature close to that of layer growth. In this case the changed layer strain was detected.

Marked inter-diffusion of components can result in creation of a buffer-like film at the layer/substrate interface during prolonged treatments (for 10 h) or at higher treatment temperature (1070 K). Hypothetical existence of such layer can be responsible for the lack of significant lattice-constant changes (as indicated by X-ray measurements). Most probably, the decrease in dislocations density (which would be caused by the presence of an additional layer at the interface) during the prolonged treatment (for 10 h) or at higher temperature (1070 K), resulted in the reduced and orientation-dependent diffuse scattering intensity. High diffuse scattering around the RSP of the substrate for the sample treated at 1070 K can be related to the creation of additional defects in the GaAs substrate.

It is necessary to point out that the distribution of diffuse scattering depended strongly on the sample orientation only for the samples treated at 0.6 GPa for 1 h at a temperature near to that of layer growth. The directional character of the diffuse scattering intensity is caused by the [$\bar{1}$10] misfit dislocations which are generated during the HT–HP treatment. The creation of the [$\bar{1}$10] misfit dislocations is the first step of strain relaxation of the layer [6, 10–12]. This phenomenon is related to enhanced mobility and decreased strain threshold for generation of

the [$\bar{1}$10] oriented dislocations in the zinc blende structure. In the next step, the dislocation network is created resulting in a change of the in-plane lattice parameter value. The pressure, for which the first step of relaxation occurs at growth temperature, is equal to 0.6 GPa, but the pressure resulting in generation of the dislocation network equals to about 1.2 GPa. For 0.6 GPa pressure, the strain of the $Al_{0.4}Ga_{0.6}As/GaAs$ sample at 920 K was calculated from the formula (5); it was equal to 1.16×10^{-3}. The critical stress for generation of [$\bar{1}$10] dislocations, equal to 0.14 GPa, was calculated from the strain–stress relation [13]. The C_{11} and C_{12} elastic constants, equal to 118.6 GPa and 60.7 GPa, respectively, were taken from [14]. It is known that stress in semiconducting heterostructures is just of this order of magnitude. So the described approach allows for more precise determination of critical stress for creation of misfit dislocations.

5. Conclusions

The relaxation of layer strain during the HT–HP treatment remains conserved after releasing the pressure and temperature to ambient conditions. This effect was more pronounced for the treatment temperature approaching that of the layer growth. When, during the treatment, the strain achieves a critical value for dislocation generations, the relaxation occurs. The critical pressure value, $HP_{\rm cr}$, at which the [$\bar{1}$110] misfit dislocations are created, was used for estimation of the critical stress value for generation of dislocations at the layer growth temperature. That critical value of stress for $Al_{0.4}Ga_{0.6}As/GaAs$ was, in our case, of about 0.14 GPa. The dislocations network was created and so the change of strain was detected for applied hydrostatic pressure between 0.6 GPa and 1.2 GPa.

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