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Optical characterization of InGaAsP/InP(001) heterostructures

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Reflectance anisotropy spectroscopy was applied for investigation of the $In_{0.8}Ga_{0.2}As_{0.5}P_{0.5}$ solid solution films. Films with a thickness of 50–1000 nm were grown on InP(001) substrates using a buffer layer of different thicknesses. It was found that during storage, samples with a buffer layer 1 μm thick can degrade. Degradation probably occurs in the region of the buffer layer and is accompanied by relaxation of internal stress in the structure. At the same time, the intensity of photoluminescence decreases, while the film surface relief does not change.

Keywords: reflectance anisotropy spectroscopy, semiconductor solid solutions $A^{III}B^{V}$, MOCVD epitaxy, built-in stress.

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The research into optical energy transmission has been on the rise lately. The use of near- and mid-IR radiation, which falls within local absorption minima, appears to be the optimum option for energy transmission through the atmosphere. A YAG:Nd laser with an operating wavelength of 1064 nm (a photon energy of 1.17 eV), which is currently used widely in various fields, may be a fitting source in this context. Solid solutions $In_xGa_{1-x}As_yP_{1-y}$ appear to be the optimum materials for photovoltaic conversion of radiation of this laser. These materials allow one to select appropriate values of band gap width E_g and crystal lattice period for growth on the available InP substrates. It is important to note that the active region of a photovoltaic converter for high-power (up to 10 kW) laser radiation must have a considerable thickness (up to 3.5 μm) and a high degree of crystalline perfection. It should also be taken into account that the $In_xGa_{1-x}As_yP_{1-y}$ solid solution system has a region of immiscibility with its dimensions depending on temperature. According to the results of our calculations reported in [1], the optimum compositions for growth at a temperature of 600°C are those with $x \approx 0.8$, $y \approx 0.5$. They have a suitable value of $E_g = 1.05$ eV and satisfy the condition of isoperiodicity with InP. The chosen compositions fall on the boundary of the spinodal decomposition region; this may make it difficult to obtain homogeneous layers with a high degree of crystalline perfection. The crystalline perfection of solid solutions $In_xGa_{1-x}As_yP_{1-y}$ also depends on the lattice mismatch (LM) between a substrate and an epitaxial film. LM induces internal stresses that may be relieved by a reconstructuring of the crystal (relaxation) [2]. The possible type of relaxation in solid solution films is largely determined by the specifics of preliminary surface preparation: the chosen substrate type, the parameters of a buffer layer, and the conditions of epitaxial growth [3–5].

In the present study, $In_xGa_{1-x}As_yP_{1-y}$ ($x \approx 0.8$, $y \approx 0.5$) films grown by metalorganic vapour-phase epitaxy (MOS hydride epitaxy) on *n*-InP(001):Sn substrates with a 4° misorientation in the (111) direction were examined. An AIXTRON AIX-200 setup was used for growth; the temperature and pressure in this process were set to 600°C and 100 mbar. Two sets of samples were studied. The first set (I297–I300) was grown on an InP buffer layer $\cong$ 1000 nm in thickness. The growth conditions for this set were detailed in [1]. The thickness of films was as follows: I297 — 50 nm, I298 — 200 nm, I299 — 500 nm, and I300 — 1000 nm. The second set (I256, I257) consisted of 1000-nm-thick films on a buffer layer with a thickness of $\cong$ 100 nm. The fluxes of precursors of $In\ _xGa_{1-x}As_yP_{1-y}$ components for sample I257 were the same as those used to grow the samples of the first set. The trimethylindium flux used for growth of film I256 was 3% lower than the one for I257. The samples were characterized by X-ray diffractometry (XRD), atomic force microscopy (AFM), and photoluminescence (PL) and reflectance anisotropy (RA) spectroscopy.

RA spectroscopy [6] is a non-destructive optical modulation technique that allows one to isolate weak anisotropic signals from the intense isotropic part of the optical response of cubic semiconductors. The RA signal for the (001) surface is the normalized difference of reflection coefficients for normally incident light: $\Delta R/R = (R_{[\bar{1}10]}R_{[110]})/R$. This technique is widely used also to determine the surface structure, estimate the band bending at interfaces, and monitor uniaxial stresses and surface relief [6,7]. In the present study, RA spectra were registrated at room temperature in air within the 1.5–5.8 eV energy range.

Figure 1, *a* presents the RA spectra of samples I297–I300 obtained immediately after growth. Note that spectral features of a small amplitude are observed in the region of energies of optical transitions E_1 and $(E_1 + \Delta_1)$ calculated

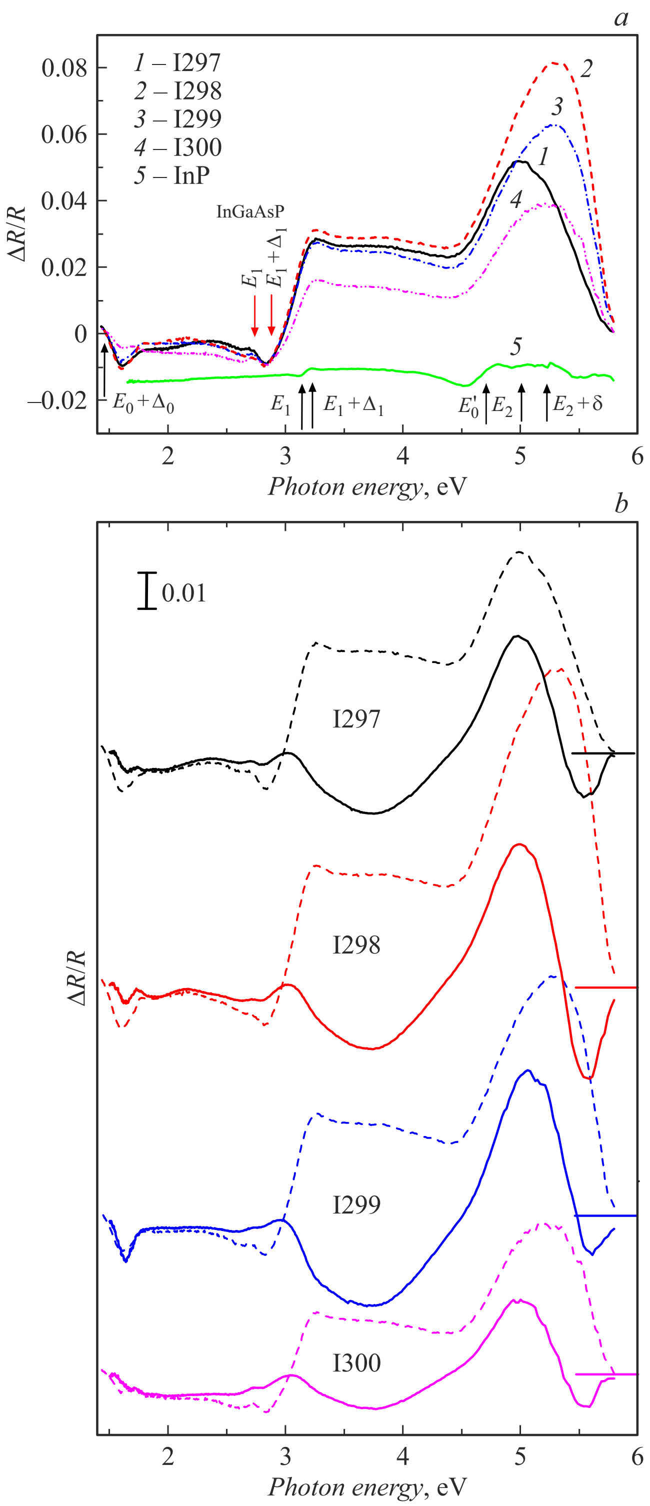

Figure 1. *a* — RA spectra of samples I297–I300 registrated immediately after growth. *b* — RA spectra registrated six months after growth (solid curves) and immediately after growth (dashed curves). Arrows indicate the energies of optical transitions for $In_{0.8}Ga_{0.2}As_{0.5}P_{0.5}$ and InP [8].

for the $In_{0.8}Ga_{0.2}As_{0.5}P_{0.5}$ composition using the formula from [8]. In the region of energies E_1, $(E_1 + \Delta_1)$ of the InP substrate, a line with a noticeably larger amplitude than in the spectrum of bulk InP(001) is seen in the spectrum of sample I297. Since the buffer layer and the film are undoped, the greater amplitude of lines may only be explained by the presence of uniaxial stress in the film and the substrate [5,6]. A feature of an unclear nature is present in the RA spectra near 1.6 eV. We believe that given the lack of phases of other compositions in the film, this feature may only be attributed to stress in the substrate region ($(E_0 + \Delta_0)$ in InP, 1.46 eV)). Thus, the observed optical anisotropy is mainly related to stress at the interface between the film and the buffer layer caused by a slight LM. According to the XRD data, the LM for sample I300 was $+2.9 \cdot 10^{-3}$.

In addition to optical transition lines, a broad structureless signal associated with the anisotropic surface relief [6,7] is presented in the RA spectra. AFM studies revealed a relief in the $[\bar{1}10]$ direction with a period of about 100 nm on the surface of all samples. An additional relief with a period of about 1 μm [2] is observed in the perpendicular direction on the surface of films with thickness 200 nm and higher. An increase in height of this relief is accompanied by a reduction in the RA signal amplitude. The emergence of a relief along [110] is associated with the relaxation of elastic stress induced by compression of the epitaxial layer.

The samples were re-examined after six months of storage in normal room conditions. A comparison of the RA spectra of films measured before and after storage (Fig. 1, *b*) reveals significant changes. The amplitude of spectral features in the region of E_1–$(E_1 + \Delta_1)$ of the solid solution decreased, but their position remained the same. This suggests that the film composition did not change. The key changes occurred in the region of optical transition energies E_1, $(E_1 + \Delta_1)$, and $E_2 + \delta$ of the InP substrate.

PL measurements performed at 77 K before and after storage of samples I297–I300 revealed a noticeable intensity reduction (Fig. 2), while the positions of the PL maxima (1.02–1.06 eV) haven't changed. XRD measurements were not repeated after storage.

Since the surface relief did not (according to the AFM data) change during storage, one may conclude that the most significant changes occurred near the film–buffer layer interface. We suppose that the reason for the observed degradation is the penetration of dislocations from the substrate into the buffer layer. It is known that dislocation nuclei in the bulk substrate layer may be inherited by the buffer layer and grow further into the solid solution film, causing plastic relaxation in it even at LM magnitudes below 10^{-3} [4]. The probability of this process depends on temperature, mechanical stress, and dislocation density of the original substrate. InP substrates,used in the present study, were czochralski-grown *n* wafers, usually characterized by dislocation densities above 10^4 cm^{-2}. According to [3], active penetration of dislocations into the structure being grown is initiated above a certain critical thickness. It may be assumed that the probability of such degradation will decrease if one uses thin buffer layers.

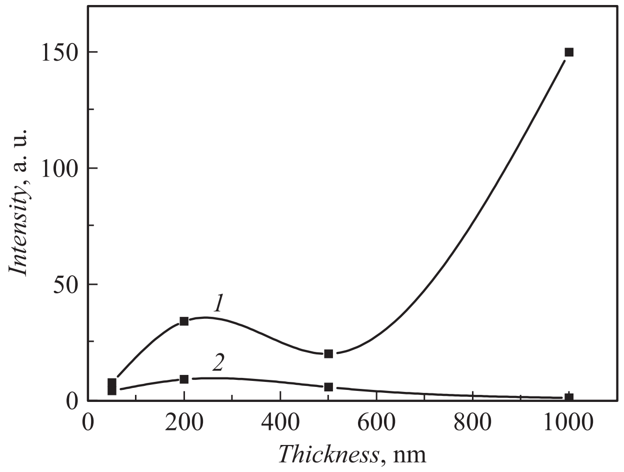

Figure 2. Dependences of the intensity of the photoluminescence maximum of samples I297–I300 on film thickness recorded immediately after growth (*1*) and several months later (*2*).

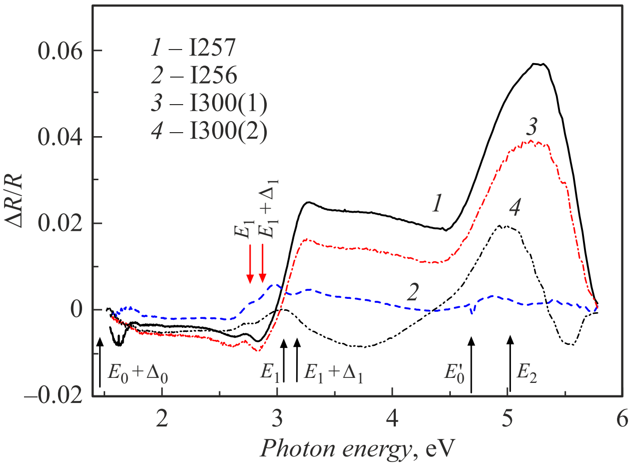

Figure 3. Comparison of RA spectra of 1000-nm-thick films grown on thin (I256 and I257) and thick (I300) buffer layers. The I300(1) and I300(2) spectra were measured immediately after and six months after growth, respectively.

To verify the validity of this assumption, we performed RA spectroscopy measurements for the I256 and I257 samples with an $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}_y\mathrm{P}_{1-y} \cong 1000$ nm layer grown on an InP buffer layer with a thickness of $\cong 100$ nm. Spectra were registrated after several years of storage of samples in air. It can be seen from Fig. 3 that the RA spectrum of sample I257 virtually matches the spectrum of sample I300 obtained immediately after growth. Thus, the levels of stress in samples I257 and 1300 are comparable. At the same time, the LM magnitude for the epitaxial layer and the substrate in I257 is lower than 10^{-3}. The probable reason for the detected stress is the rearrangement of the buffer layer–film interface during pre-growth annealing.

Samples I300 and I256 have LMs close in magnitude and differing in sign: $2.9 \cdot 10^{-3}$ for I300 and $-2.1 \cdot 10^{-3}$ for I256. The RA spectrum of sample I256 (Fig. 3) grown on a 100-nm-thick buffer layer differs greatly from the I300(1) and I257 spectra. It is more similar to the I300(2) spectrum registrated after six months of storage. In contrast to the I300(2) spectrum, the lines associated with optical transitions $E_1-(E_1+\Delta_1)$ in the InP substrate are not broadened in the spectrum of sample I256; the amplitudes of RA lines in the region of transitions $E_0+\Delta_0$, $E_0'-E_2$ are small. Thus, we can assume that the near-interface substrate region is not damaged in I256. Moreover, I256 reveals no stress, just as I300(2), We believe that the stress relaxation in sample I256 occurred directly in the growth process (primarily in the solid solution region).

To conclude, we note that the optical RA technique turned out to be efficient in characterizing the $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}_y\mathrm{P}_{1-y}$/InP (001) heterostructures. It was found that the probability of stress relaxation during film growth on a thick buffer layer is lower. However, subsequent degradation of the sample as a result of destruction of the buffer layer is possible in this case. The use of higher-quality substrates and modification of the pre-growth surface preparation procedure, along with the buffer layer growth parameters, may help to prevent such degradation.

Conflict of interest

The authors declare that they have no conflict of interest.

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