Structural and optical properties of epitaxial Ga$_x$In$_{1-x}$P alloys with atomic ordering

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Abstract. A range of structural and spectroscopic techniques were used for the study of the properties of epitaxial Ga$_x$In$_{1-x}$P alloys with an ordered arrangement of atoms in a crystal lattice grown by MOCVD on GaAs (100). The appearance of atomic ordering in the coherent growth conditions of the ordered Ga$_x$In$_{1-x}$P alloy resulted in cardinal changes of the structural and optical properties of semiconductor in comparison to disordered alloys, including the change of the crystal lattice parameter and, consequently, reduced crystal symmetry, decreased band gap and formation of two different types of surface nanorelief. Based on the variance analysis data with regard to the IR-reflection spectra as well as the UV-spectroscopy data obtained in the transmission-reflection mode, the main optical characteristics of the ordered Ga$_x$In$_{1-x}$P alloys were determined for the first time, namely, refractive index dispersion and high-frequency dielectric constant.

1. Introduction

Alloys based on A$_x$B$_y$ semiconductors have attracted the interest of researchers of semiconductor optoelectronics cause they have a positive formation enthalpy that facilitates superstructure ordered phases on the basis of these alloys [1–3]. This phenomena of the ordering appearance in A$_x$B$_y$ allows the inclusion of narrow-band semiconductors in a wide-band gap matrix and vice versa, thus creating a localizing potential for the current carriers. Furthermore, the spontaneous appearance of the nanostructures provides a basis for a new technology for the production of ordered arrays of irregularities, moreover, the basis for the next generation opto- and microelectronics [1,4]. The urgent problem of atomic ordering is firstly connected with the modification of the fundamental properties of semiconductor systems caused by the change of symmetry of the crystalline structure [4,5]. However, to date the findings only confirm the theoretical data regarding the change in band gap for alloys with an ordered arrangement of the atoms dependent on the composition and degree of ordering. There is a lack of information on the optical properties of Ga$_x$In$_{1-x}$P alloys with ordering in IR and UV spectral ranges for the epitaxial alloys, as well as the direct data and the values of parameters for the crystal lattice in the ordered Ga$_x$In$_{1-x}$P alloys dependent on the degree of ordering and conditions of epitaxial growth. For this reason, the aim of this study was to investigate the structural and optical properties of epitaxial Ga$_x$In$_{1-x}$P alloys with atomic ordering grown by MOCVD in a coherent way on GaAs (100) substrates.

2. Objects and Methods of Investigations

Epitaxial layers of Ga$_x$In$_{1-x}$P with ordering matched by the parameter of the crystal lattice with single-crystalline GaAs (100) substrates were grown by MOCVD in a horizontal reactor under a pressure of 60 mbar. The reactants for III group elements were tri-methyl gallium (TMG) and tri-methyl indium (TMI), and the reactant for the V group element was phosphine in a 10% mixture with hydrogen. Ga$_x$In$_{1-x}$P layers with a composition of x ~ 0.50 were grown on semi-insulating substrates of GaAs (100), misoriented by 2° relative to the direction of [110], with epitaxial films ~ 1 µm thick. The technological growth parameters are presented in Table 1.
Table 1. Parameters of growth and thickness of the epitaxial layers in the samples of heterostructures with ordering in the alloy.

| Sample | Growth temperature, °C | V/III ratio | Thickness, μm |
|--------|------------------------|-------------|--------------|
| #S1    | 700                    | 160         | 1            |
| #S2    | 650                    | 100         | 1            |
| #S3    | 600                    | 135         | 0.85         |

The structural quality of the heterostructures were performed by X-ray diffraction. The IR reflection spectra of the samples were obtained with the use of spectrometer Vertex-70 Bruker. The study of the surface morphology was performed by AFM. PL spectra were obtained from the samples according to the standard technique, with the use of a monochromator TRIAX550 and CCD detector and 514.5 nm excitation wavelength. The optical properties in the range of 190–900 nm were studied using a LAMBDA 650.

3. Experimental Results and Discussion

3.1. Structure investigations

Experimental profiles of X-ray diffraction from 400 planes for the investigated heterostructures are presented in Figures 1.a – d by the solid lines. As seen from the figures, reflections from the single-crystalline substrate and the alloy can be clearly observed in all the diffraction patterns; clearly, the diffraction from the ordered alloy is characterized by the different angle position. Taking into account that all of the investigated GaIn1−xP alloys were actually of the same composition, it was assumed that the essential differences in the interplanar distances are probably due to a different degree of ordering in the epitaxial film.

![Figure 1](image)

Figure 1. Experimental profiles of X-ray diffraction obtained from (400) plane of the ordered GaIn1−xP/GaAs(100) heterostructures as well as the results of profiles decomposition over components.

Table 2. Experimental and calculated data obtained on the basis of results of X-ray diffraction and microanalysis.

| Sample | Perpendicular deformation ε⊥ | The ratio of the half-widths FWHM_{GaInP} / FWHM_{GaAs} | Long range order parameter η calculated from [2] | Atomic content calculated from XRD and Zunger data [2] |
|--------|-------------------------------|------------------------------------------------------|--------------------------------------------------|-----------------------------------------------------|
| #S1    | 0.0003                        | 1.11                                                 | 0.50                                             | ~0.51                                               |
| #S2    | 0.001                         | 1.61                                                 | 0.50                                             | ~0.50                                               |
| #S3    | 0.003                         | 2.01                                                 | 0.60                                             | ~0.50                                               |

The calculated lattice parameters in accordance with the linear elasticity theory [6,7] taking into account the internal stresses in heteropeitaxial layer a’ and half widths of the diffraction lines are presented in Table 2. It is quite clear that these parameters do not coincide, which is due to the change in the structure of the alloy under atomic ordering in the metallic sublattice. Calculated perpendicular deformations in GaIn1−xP films for the samples investigated in this work are presented in Table 2.
3.2. Atomic force microscopy

It is well known that the epitaxial growth of Ga$_x$In$_{1-x}$P alloys with an ordering in the crystal lattice is often accompanied by formation of close-packed clusters on the surface of the epitaxial film [5,8]. Therefore, the morphology and phase distribution was investigated on the surface of the samples of Ga$_x$In$_{1-x}$P/GaAs (100) heterostructures with ordering in the alloy using atomic-force microscopy (AFM). Figure 2 represents 3D images of the characteristic areas in the heterostructures.

The results of AFM demonstrated that the areas of the ordered ridge-shaped nanorelief oriented along a single direction are present on the surface of the epitaxial film for the samples #S1 and #S2. The ordering period of nanorelief for the samples of #S1 and #S2 is ~50 – 75 nm for the mean relief height of 5 – 10 nm. The phase contrast data showed that only one phase was present on the surface of these samples, Ga$_x$In$_{1-x}$P alloy with an ordering. Unlike the first two samples on the surface of heterostructure #S3 the areas with the ordered nanorelief are not observed. However, one can observe the appearance of an array of nano-sized non-uniformities in the form of islets on the surface of the epitaxial film. The composition of the nanoislets, according to the phase contrast data, differs from the matrix composition of the Ga$_x$In$_{1-x}$P matrix. The characteristic size of the non-uniformities is 20 – 50 nm in diameter and 10 – 15 nm in height.

3.3. IR-spectroscopy

IR-spectroscopy technique is widely used for studies of fine lattice properties and estimation of the structural quality of epitaxial films. It allows the estimation of internal stresses in the crystal lattice, since this method is very sensitive to the stresses. The IR reflection spectra for all of the heterostructures demonstrate longitudinal LO and transverse TO phonon modes of Ga – P and In – P vibrations characteristic for Ga$_x$In$_{1-x}$P alloy, in agreement with data previously reported [9]. However, additional phonon vibrations were observed in the range of 200 – 220 cm$^{-1}$ in the spectrum of sample #S3, which according to the data of theoretical calculations taken from [9], belong to the vibrations of an ordered alloy with a large order factor $\eta$. Moreover, the frequencies of the basic phonon modes for the samples #S1 and #S2 are quite close, while for sample #S3, the shift of the phonon vibration frequencies to the low-frequency range is observed (see Figure 3).

In addition, a noticeable splitting of the frequency bands can be clearly seen. During modelling of IR-reflection spectra for the lattice vibrations in heterostructures, these spectra can be calculated in the model “film-substrate”, as described in our previous studies [10–12]. This model makes it possible to perform dispersion analysis of the IR reflection spectra taking into account the phonon modes appearing in the film, as in the
substrate. The value of high-frequency dielectric permeability \( \varepsilon_\infty \) for epitaxial Ga\(_x\)In\(_{1-x}\)P alloy with the ordering determined in the dispersion analysis as well as with the use of Kramers-Kronig relation is also presented in Table 3.

### Table 3. Results of dispersion analysis for IR reflection spectra and photoluminescence spectroscopy for the investigated samples.

| Sample | High-frequency dielectric permeability | Experimental PL energy at 300 K, eV | Calculated for \( \varepsilon_\infty \) PL energy at 300 K, eV | Long range order parameter \( h \) from [2] |
|--------|--------------------------------------|-----------------------------------|---------------------------|------------------|
| #S1    | 16.2                                 | 1.841                             | 1.893                     | 0.50             |
| #S2    | 17.3                                 | 1.845                             | 1.893                     | 0.50             |
| #S3    | 12.5                                 | 1.831                             | 1.885                     | 0.60             |

#### 3.4. PL spectroscopy

As noted above, the appearance of atomic ordering in the Ga\(_x\)In\(_{1-x}\)P alloy inevitably affects its energy characteristics by changing the band gap as compared with the disordered alloy of similar composition [5,8,13]. So, the application of photoluminescence spectroscopy as a tool for the determination of band gap changes and the influence of the ordering degree in the alloy on the band gap value is appropriate. Experimental photoluminescence spectra for the samples are presented in Figure 4.

![Figure 4. Experimental photoluminescence spectra of epitaxial ordered Ga\(_x\)In\(_{1-x}\)P/GaAs(100) heterostructures.](image)

Emission from the ordered Ga\(_x\)In\(_{1-x}\)P alloy for all samples appears as a peak with a half-width of \( \Delta \sim 0.05\text{eV} \). It should be noted that the intensity of photoluminescence for sample #S3 exceeds the intensity of the #S1 and #S2 samples by more than 1.5 – 2 times. The experimental values of \( E_g \) are presented in Table 3, as well as the values of the band gap for disordered Ga\(_x\)In\(_{1-x}\)P alloys of similar composition determined in [14]. From the data in Table 4, it is evident that the value of the band gap energy for the epitaxial film of each sample is less than it should be in case of a disordered alloy of similar composition. Based on the theoretical calculations reported by Zunger et al. [2] in combination with the value of band gap energy determined in this experimental study, the values of the coefficients of the perpendicular distortion (the value of elastic stresses) and parameter \( \Delta E_g \) (decrease of the band gap value), it was possible to specify the degree of ordering in the Ga\(_x\)In\(_{1-x}\)P alloy grown on GaAs (100) (see Table 3). This data is in good agreement with the similar data from [13].

#### 3.5. UV spectroscopy

In our previous studies [15,16], the use of surveying spectra technique in reflection mode within ultraviolet and visible ranges of electromagnetic emission was shown to be a convenient approach for the study of the optical properties of thin semiconductor and dielectric films. Using the experimental data obtained from the analysis of maximums and minimums in the transmission-reflection spectra for two different incidence angles, it is possible not only to determine refractive index of the film in the sample but also to calculate dispersion of the refractive coefficient in rather wide interval of the angles. The calculated values (points) of the refractive coefficient for the investigated Ga\(_x\)In\(_{1-x}\)P/GaAs structures and the dependences approximated by splines are presented in Figure 5.
4. Discussion of the obtained results

Based on the XRD data (Figure 1, Tables 1 & 2), one can conclude that growth of the Ga$_{1-x}$In$_x$P alloy with ordering within the range of compositions ($x \sim 0.50$) that provides matching of the parameters of the epitaxial film and a single-crystalline GaAs (100) substrate results in the appearance of elastic stresses in the alloy. This is due to changes in the crystal lattice parameter in the ordered alloy in comparison with that of the disordered alloy with a similar composition. Furthermore, the effects of atomic ordering and distortion (elastic stresses) result in the appearance of the areas with the gradient of composition in the epitaxial film, as well as the formation on the surface of the film either of areas with the ordered nanorelief, or an array of nano-size irregularities with a composition different from the composition of the matrix (Ga$_{1-x}$In$_x$P alloy). With an increase in the ordering factor (long-range order) at the invariable composition of the alloy, the tetragonal distortion also increased, since it is due to the growth of a crystal lattice parameter in the ordered alloy. An increase in the elastic stresses results in the modification of the shape of the epitaxial film surface. Consequently, at low values of the order/distortion factor, the areas of ordered nanorelief predominate the surface of the film (see Figure 2). The maximum values of the order/distortion factor lead to the formation of an array of nano-size irregularities on the surface. According to the IR-spectroscopy data, it is not only the changes in the frequencies for the main phonon modes that are observed in the spectrum of the ordered alloy with a high degree of order in comparison with disordered alloy of similar composition, but also some additional phonon modes appear shifted towards the low-frequency range. This is in good agreement with the theoretical representations on the vibrational spectra in Ga$_{1-x}$In$_x$P alloys with ordering and they also coincide with similar data for the ordered Al$_{0.50}$Ga$_{0.50}$As alloys [12,17]. Comparing the value of high-frequency dielectric permittivity $\varepsilon_0$ for the epitaxial ordered Ga$_{1-x}$In$_x$P alloys with that for the disordered alloys of the same composition $x \sim 0.50$ [18] determined from the analysis of IR reflection spectra, it was for the first time shown that this parameter for the ordered alloy was $1.5 \sim 2$ times higher (see Table 3). The study of the optical and photoluminescence properties of the ordered Ga$_{1-x}$In$_x$P alloys in the UV spectral range confirms previous data that the MOCVD not only gives rise to a strong CuPt-B type ordering but also ensures a good uniformity of the film and its transmission capacity. A decrease in the band gap energy on the ordered Ga$_{1-x}$In$_x$P alloy determined in our experiments at the specified level of distortion and factor of the order is in good agreement with the theoretical data [2]. A decrease in the epityx temperature from 700 to 600°C increased the degree of order in Ga$_{1-x}$In$_x$P alloys, enhanced intensity of photoluminescence and also reduced the band gap value. However, none of the previously performed investigations provided any information on the dispersion of the refractive coefficient in the ordered Ga$_{1-x}$In$_x$P alloys. Based on the results of our calculations obtained from the direct experimental data, it was shown for the first time (see Figure 5) that the refractive index for the epitaxial films with ordering is 1.5 – 2.5 times higher than that for disordered values of the same composition $x \sim 0.50$. Moreover, the maximum value of refractive index for the sample with a high degree of order was $n = 5.45$ at the wavelength of $\sim 680$ nm, while the close value for the disordered alloy with a similar composition of $x \sim 0.50$ was attained in the wavelengths in the range of $\sim 330 \sim 340$ nm [18].

In summary, the findings from this study confirm the perspectives and possibilities for engineering of the band gap in heterostructures by combining the effects of tetragonal distortion under epitaxial growth with the effects of atomic ordering.

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References

[1] Zunger A 1997 Spontaneous Atomic Ordering in Semiconductor Alloys: Causes, Carriers, and Consequences MRS Bull. 22 20–6
[2] Wei S-H and Zunger A 1994 Optical properties of zinc-blende semiconductor alloys: Effects of epitaxial strain and atomic ordering Phys. Rev. B 49 14337–51
[3] Lee H S and Lee J Y 2003 CuAu-I-type ordered structures in InxAl1−xAs epilayers grown on (001) InP substrates Appl. Phys. Lett. 82 2999–3001
[4] Seredin P V, Domashevskaya P, Arsenteyv I N, Vinokurov D A, Stankevich A L and Prutskij T 2013 Superstructured ordering in AlxGa1−xAs and GaNx1−xP alloys Semiconductors 47 1–6
[5] Ahrenkiel S P, Jones K M, Matson R J, Al-Jassim M M, Zhang Y, Mascarenhas A, Friedman D J, Arent D J, Olson J M and Hanna M C 1999 CuPt-B Ordered Microstructures in GaInP and GaInAs Films MRS Proc. 583
[6] Zhou D and Usher B F 2001 Deviation of the AlGaAs lattice constant from Vegard’s law J. Phys. Appl. Phys. 34 1461–5
[7] Seredin P V, Glotov A V, Ternovaya V E, Domashevskaya E P, Arsenteyv I N, Vavilova L S and Tarasov I S 2011 Spinodal Decomposition of GaIn1−xAsP1−y Quaternary Alloys Semiconductors 45 1433–40
[8] Gomyo A, Suzuki T and Iijima S 1988 Observation of Strong Ordering in GaIn1−xP alloy semiconductors Phys. Rev. Lett. 60 2645–8
[9] Pagès O, Chafi A, Fristot D and Postnikov A V 2006 (Ga,In)P: A standard alloy in the classification of phonon mode behavior Phys. Rev. B 73 165206
[10] Verleur H W 1968 Determination of Optical Constants from Reflectance or Transmittance Measurements on Bulk Crystals or Thin Films J. Opt. Soc. Am. 58 1356
[11] Domashevskaya E P, Seredin P V, Arsenteyv I N, Vinokurov D A, Tarasov I S and Zhurbina I A 2010 The substructure and luminescence of low-temperature AlGaAs/GaAs(100) heterostructures Semiconductors 44 184–8
[12] Domashevskaya E P, Seredin P V, Lukin A N, Bityutskaya L A, Grechkina M V, Arsent’ev I N, Vinokurov D A and Tarasov I S 2006 Infrared reflectance spectra and morphologic features of the surface of epitaxial AlxGa1−xAs/GaAs(100) heterostructures with the ordered AlGaAs2 phase Semiconductors 40 406–13
[13] Ernst P, Geng C, Scholz F and Schweizer H 1996 Ordering in GaInP2 studied by optical spectroscopy Phys. Status Solidi B 193 213–29
[14] Adachi S 2009 Properties of semiconductor alloys: group-IV, III-V and II-VI semiconductors (Chichester, U.K: Wiley)
[15] Seredin P V, Lenshin A S, Kashkarov V M, Lukin A N, Arsentiev I N, Bondarev A D and Tarasov I S 2015 Ultrathin nano-sized Al2O3 strips on the surface of por-Si Mater. Sci. Semicond. Process. 39 551–8
[16] Seredin P V, Kashkarov V M, Arsentiev I N, Bondarev A D and Tarasov I S 2016 Distinctions of the growth and structural-spectroscopic investigations of thin AlN films grown on the GaAs substrates Phys. B Condens. Matter 495 54–63
[17] Domashevskaya E P, Seredin P V, Lukin A N, Bityutskaya L A, Grechkina M V, Arsentiev I N, Vinokurov D A and Tarasov I S 2006 XRD, AFM and IR investigations of ordered AlGaAs2 phase in epitaxial AlxGa1−xAs/GaAs(100) heterostructures Surf. Interface Anal. 38 828–32
[18] Schubert M, Gottschalch V, Herzinger C M, Yao H, Snyder P G and Woollam J A 1995 Optical constants of GaIn1−xP lattice matched to GaAs J. Appl. Phys. 77 3416