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Experimental investigations of atomic ordering effects in the epitaxial $Ga_xIn_{1-x}P$, coherently grown on GaAs (100) substrates

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ABSTRACT

A range of structural and spectroscopic techniques were used for the study of the properties of epitaxial $Ga_xIn_{1-x}P$ alloys with an ordered arrangement of atoms in a crystal lattice grown by MOCVD on single-crystalline substrates of GaAs (100). The appearance of atomic ordering in the coherent growth conditions of the ordered $Ga_xIn_{1-x}P$ alloy on GaAs (100) 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.

This is the first report of the calculation of parameters of the crystal lattice in $Ga_xIn_{1-x}P$ with ordering taking into account the elastic stresses dependent on long-range ordering. 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 $Ga_xIn_{1-x}P$ alloys were determined for the first time, namely, refractive index dispersion and high-frequency dielectric constant. All of the experimental results were in good agreement with the previously developed theoretical beliefs.

1. Introduction

Alloys based on A_3B_5 semiconductors have attracted the interest of researchers of semiconductor optoelectronics. These alloys are characterized by a positive formation enthalpy that facilitates superstructure ordered phases on the basis of these alloys, with formation of a domain structure under certain technological conditions [1–3]. The spontaneous appearance of periodically ordered structures on the surface and in the epitaxial films of A_3B_5 semiconductors covers a broad range of phenomena in solid state physics and semiconductor technology, specified by the processes of self-organization in the condensed matter. This is of particular interest for the production of semiconductor nanostructures with typical sizes of ≤100 nm [4]. This phenomena of the ordering appearance in A_3B_5 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. Periodical structures of these inclusions can form superlattices comprised of quantum wells, wires or quantum dots. 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].

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 in A_3B_5 compounds [5,6]. These include the observed change of the band gap in a semiconductor, the transition from indirect to direct band gap material, an inverse order of the band arrangement, and complication of the optical spectra in superstructure phases as a result of electronic states splitting near the valence band top and conduction band bottom [2,7].

It is well-known that spontaneous ordering in A_3B_5 semiconductors gives rise to a decrease in the band gap and splitting of the valence band maximum. Similar effects can be due to the elastic stresses of mismatch in the crystal lattices under epitaxial growth. The appearance of the elastic stresses caused valence band splitting and depending on the sign, results in an increase or decrease of the band gap in a semiconductor layer. A theory explaining the deformation occurring due to the mismatch of the crystal lattice parameters between the

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epitaxial layer and a substrate initiating the above-presented phenomena was described by Zunger and Wei [2,8]. They demonstrated that the ordering in the crystalline lattice and the following clusterization resulted in a decrease of the band gap.

It was suggested that the ordering in semiconductors could considerably enhance the degree of spin polarization of photoelectrons released from the valence band. Hence, this type of semiconductor alloy based on A_3B_5 compounds can be used as a source of polarized electrons, providing new opportunities for engineering the band gap in heterostructures by combining the effects of tetragonal distortion under epitaxial growth with the effects of atomic ordering.

It should be noted that well-developed theoretical ideas on the effects concerned with the atomic ordering quite often lack experimental support. Therefore, the effect of ordering for the alloy systems of $Al_xGa_{1-x}As$, $Ga_xIn_{1-x}P$, and $Ga_xIn_{1-x}As_yP_{1-y}$ rather sufficiently matched with single-crystalline substrates of GaAs (100) is considered to be of high practical importance.

A review of the literature revealed that the main experimental investigations of appearance of the atomic ordering were performed for the $Ga_xIn_{1-x}P$ system, where this phenomenon was observed for the first time. 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 [4,7,9]. The main experimental methods used were electron microscopy/diffraction for the detection of the ordering within an alloy and photoluminescence spectroscopy for the estimation of the changes in the electron band structure. However, there is a lack of information on the optical properties of $Ga_xIn_{1-x}P$ 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 $Ga_xIn_{1-x}P$ 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 $Ga_xIn_{1-x}P$ alloys with atomic ordering grown by MOCVD in a coherent way on GaAs (100) substrates.

2. Objects and methods of investigations

Epitaxial layers of $Ga_xIn_{1-x}P$ 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. $Ga_xIn_{1-x}P$ 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.

The structural quality of the heterostructures and determination of the lattice parameters in the alloys were performed by X-ray diffraction with an X-ray diffractometer DRON 4–07 and characteristic radiation of cobalt. The IR reflection spectra of the heterostructures were obtained with the use of an IR-Fourier spectrometer Vertex-70 Bruker. The study of the surface morphology was performed by atomic-force microscopy using a NTEGRA Therma (NT MDT) microscope. The concentration of the elements in the alloys was refined by X-ray microanalysis using an Oxford Instruments attachment to the electron microscope JEOL.

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

Photoluminescence spectra were obtained from the surface of the samples according to the standard technique, with the use of a monochromator TRIAX550 and CCD detector cooled with liquid nitrogen. Excitation of photoluminescence spectra was performed with the use of an argon laser with a wavelength of 514.5 nm. Laser emission was focused on the surface with 10x objective.

The optical properties of $Ga_xIn_{1-x}P$ layers were studied within the range of 190–900 nm by UV-spectroscopy using a LAMBDA 650 spectrometer produced by Perkin Elmer Company, supplied with a universal reflection attachment URA, which makes it possible to obtain reflection spectra within the range of the incidence angles from 8° to 80°. In addition, the operating scheme of the attachment allows the absolute reflection to be obtained. Reflection spectra were obtained at different incident angles within the range of 8–67°.

3. Experimental results and discussion

3.1. Structure investigations

The concentration of the elements comprising the $Ga_xIn_{1-x}P$ alloys were specified with high precision using X-ray microanalysis and an attachment to the electron microscope JEOL. It should be noted that the depth of analysis for this method is considerably greater than the thickness of the epitaxial film (~1 μm); hence, the concentration data may include a small error since both the alloy and single-crystalline substrate contain gallium atoms. However, this error can be excluded by a series of one-type samples with small changes in the element concentrations. Assuming that the change in the calculated concentration of an element in the alloy will have a similar effect on the microanalysis results, one can determine the contribution of the atoms in the substrate to the microanalysis data, thereby introducing the necessary corrections. As seen from the X-ray microanalysis data in Table 2, all of the alloys were grown near the point of half-composition, x~0.50 ± 0.01.

The study of the structural quality of the $Ga_xIn_{1-x}P$/Ga (100) samples with ordering was performed by X-ray diffraction. The accuracy of determining the interplanar distances and lattice parameters was ~0.0001 Å. Experimental profiles of X-ray diffraction from 400 planes for the investigated heterostructures are presented in Fig. 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 $Ga_xIn_{1-x}P$ 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.

Crystal lattice parameters for the alloys were calculated to determine the changes in the crystal lattice of the epitaxial $Ga_xIn_{1-x}P$ films with an ordered arrangement of the atoms in the metallic sublattice. The lattice constant taking into account the elastic stresses in the heteroepitaxial layer a^{ν} in accordance with the linear elasticity theory [10,11] were calculated as follows:

$$a^{\nu} = a^{\perp}\frac{1-\upsilon}{1+\upsilon} + a^{\parallel}\frac{2\upsilon}{1+\upsilon} \quad (1)$$

Where, ν - are Poisson coefficients for the epitaxial layers, $a^{\perp}$ and $a^{\parallel}$ are perpendicular and parallel components of the lattice parameters.

Since the coherent growth of the $Ga_xIn_{1-x}P$ alloy on the single-crystalline GaAs (100) substrate parallel component of the epitaxial layer $a^{\parallel}$ can be replaced by the crystal lattice parameter of GaAs:

$$a^{\parallel} = a_{GaAs} = 5.6532\text{Å}$$