Superstructured Ordering in Al$_x$Ga$_{1-x}$As and Ga$_x$In$_{1-x}$P Alloys

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Abstract—Epitaxial heterostructures produced on the basis of Al$_x$Ga$_{1-x}$As and Ga$_x$In$_{1-x}$P ternary alloys by metal–organic chemical vapor deposition are studied. The composition parameter $x$ of the alloys was ~0.50. By X-ray diffraction studies, scanning electron microscopy, atomic force microscopy, and photoluminescence spectroscopy, it is shown that superstructured ordered phases with the stoichiometry composition \( \text{III}_1 - n\text{II}_1 + n\text{V}_2 \) can be formed. As a consequence of this effect, not only does the cubic crystal symmetry change to the tetragonal type in the new compound, but also the optical properties become different from those of disordered alloy with the same composition.

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1. INTRODUCTION

It is well known that structural ordering is a topical problem since ordering is directly accompanied by modification of the fundamental properties of semiconductor systems through lowering of the zincblende structural symmetry of III–V compounds. The results of this effect are possible changes in the band gap, transformation of an indirect-gap semiconductor into a direct-gap semiconductor, inversion of the order of energy–band arrangement, and the formation of more complex optical spectra of superstructured phases as a result of the removal of the degeneracy of states corresponding to the top of the valence band and the bottom of the conduction band.

An overview of currently available publications [1–5] shows that there exist a large number of disembodied data on experimentally observed spontaneous ordering and the formation of nano-scale irregularities in III–V alloys, as well as on the possibilities of producing photoelectric and optoelectronic devices, whose operation is based on controllable self-assembly and superstructure formation in epitaxial III–V semiconductor alloys. However, the well-developed theoretical concepts [1, 2] are often not supported experimentally, and therefore, the effect of ordering in alloys, such as the Al$_x$Ga$_{1-x}$As, Ga$_x$In$_{1-x}$P, and Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$ systems rather well matching in lattice parameters with GaAs (100) single-crystal substrates, is currently of great interest and practical importance.

What are the special features of the above-mentioned ordered three-dimensional (3D) configurations? It is found that some of them exhibit a unique topological property: these configurations possess sufficient degrees of structural freedom to adjust to any bond length and bond angle, including an ideal length and angle. This is caused by the fact [1, 2] that certain ordered 3D atomic configurations minimize the energy of strains generated as a result of lattice mismatch between the constituent compounds of the alloy, whereas a random atomic arrangement does not provide such minimization. Obviously, the point is that, in strained systems, different atomic configurations can have quite different enthalpies with the atomic composition being the same. An ordered atomic arrangement corresponds to a thermodynamically stable structure for several atomic layers located near the surface. Further, deeper in the film, the thermodynamically stable structure returns either to a two-phase system with separated phases [3] (if the film is incoherent) or to the ordered chalcopyrite structure [4] (if the film is coherent). Thus, if we assume that the ordered structure stable at the surface is capable of extending deep into the film (mainly through decomposition of the alloy into separate phases or through ordering with the chalcopyrite formation), we must concede that, if the film is covered by several monolayers of incident atoms, the ordered structure looks as if it is frozen into the film. In other words, the atomic ordering near the surface is of thermodynamic nature, whereas the extension of ordering deep into the film is
consistent general potential method in the linearly theoretically in [6, 7]. In these calculations, the self-ordering, which ordering is of the CuAu-I type, were studied and electron density. For example, for the Al changes occur in the band gaps, spin–orbit splitting, possible to show that, for such systems, dramatic electronic properties of semiconductor alloys [7], it was possible to show that, for such systems, dramatic changes occur in the band gaps, spin–orbit splitting, and electron density. For example, for the Al$_{1-x}$Ga$_x$As alloy ordered according to CuAu-I in the (100) direction, the shift of the conduction level is expected to be 0.15 eV. The electronic and positron band structure of the tetragonal AlGaAs$_2$ compound which crystallizes with the formation of the CuAu-I-like structure was also theoretically studied in [6]. The calculation performed in [6] was based on the full potential (FP) LAPW method and the DFT method. It was shown that the tetragonal Al$_{1-x}$Ga$_x$As alloy was bound to be an indirect-gap material or a direct-gap material at low values of the composition parameter $x$, or at large values of the parameter ($x > 0.45$). This is due to the band bending and band mixing effects in ordered layers which essentially consist of direct-gap GaAs and indirect-gap AlAs binary compounds. The calculations carried out in [6] show that the AlGaAs$_2$ compound is a pseudo-direct-gap semiconductor. In the case under consideration, a pseudo-direct-gap semiconductor is such that the interband transition is direct, but nominally corresponds to a low-probability, i.e., an almost forbidden optical transition for the CuAu-I-type structure.

In contrast to ordering in Al$_{1-x}$Ga$_x$As alloys, this phenomenon of ordering in Ga$_x$In$_{1-x}$P alloys (at $x \approx 0.50$) is better understood. Using finished devices as an example, Ahrenkiel [8] reported on the effects of ordering on the optoelectronic properties of these materials, specifically, on narrowing of the band gap, the appearance of birefringence, the appearance of anisotropy of the charge-carrier mobility, and an increase in the charge-carrier lifetime. In this case, ordering in the Ga$_{1-x}$In$_x$P alloy can be described as the formation of a CuPt-B-type lattice (Fig. 1). Ordering in the Ga$_{1-x}$In$_x$P alloy is of kinetic origin. Metal-organic chemical vapor deposition (MOCVD) not only favors the efficient CuPt-B-type ordering, but provides a high degree of homogeneity of the film and of its transparency as well. It is shown that the ordered GaInP alloy on a GaAs (111) substrate is bound to exhibit a broad distribution of differently sized domains on the surface. The antiphase boundaries of the ordered phase are often oriented in the opposite direction with respect to the plane of growth, as compared to the direction of growth of GaInP. This phenomenon is controlled by the surface-diffusion rate and the density redistribution.

Thus, we can state that atomic ordering is typical of three-component III–V semiconductor compounds with the composition parameter $x \approx 0.50$ and provides new optical and electrical characteristics compared to those of disordered alloys. The production of ordered alloys based on III–V semiconductors is of considerable practical interest, since the alloys can serve as the basis for a new generation of optoelectronic and nanoelectronic devices. In this paper, we present the continuation of a series of studies concerning ordering in epitaxial Al$_{1-x}$Ga$_x$As and Ga$_{1-x}$In$_x$P ternary alloys and report the results of experimental investigations into the properties of the superstructure phases formed upon structural ordering.

**Fig. 1.** Structural forms of ordered isovalent semiconductor alloy crystals: (left) the InGaAs$_2$ and (right) CuPt-B types.

controlled by the kinetic of growth of the ordered structure [5].

Laref et al. [6] were the first to theoretically consider the properties of the Al$_{1-x}$Ga$_x$As alloy in the form of an AlGaAs$_2$ superstructure phase by using the linearized augmented plane waves (APW) method. The calculation was carried out for the Al$_{1-x}$Ga$_x$As alloy formed as an ordered CuAu-I-type superstructure, in which the arrangement of anions in the unit cell is the same as that in the zinc-blend structure, but differs from it by the ordered arrangement of cations. As in the case of the layered tetragonal InGaAs$_2$ superstructure (Fig. 1), the ordering of cations makes the alloy structure tetragonal along the $c$ axis. In [6], it is shown that, for the AlGaAs$_2$ structure with CuAu-I-type ordering, the lattice parameters in the plane of growth and in the direction of growth are $a = 5.6399$ Å and $a^\perp = 5.6413$ Å, respectively.

The electronic properties of Al$_{1-x}$Ga$_x$As alloys, in which ordering is of the CuAu-I type, were studied theoretically in [6, 7]. In these calculations, the self-consistent general potential method in the linearly augmented plane waves (LAPW) approximation and the density functional theory (DFT) in the local density approximation (LDA) were used. On the basis of the theory of ordering-induced changes in the electronic properties of semiconductor alloys [7], it was possible to show that, for such systems, dramatic changes occur in the band gaps, spin–orbit splitting, and electron density. For example, for the Al$_{1-x}$Ga$_x$As superlattice ordered according to CuAu-I in the (100) direction, the shift of the conduction level is expected to be 0.15 eV. The electronic and positron band structure was also theoretically studied in [6]. The calculation performed in [6] was based on the full potential (FP) LAPW method and the DFT method. It was shown that the tetragonal Al$_{1-x}$Ga$_x$As alloy was bound to be an indirect-gap material or a direct-gap material at low values of the composition parameter $x$, or at large values of the parameter ($x > 0.45$). This is due to the band bending and band mixing effects in ordered layers which essentially consist of direct-gap GaAs and indirect-gap AlAs binary compounds. The calculations carried out in [6] show that the AlGaAs$_2$ compound is a pseudo-direct-gap semiconductor. In the case under consideration, a pseudo-direct-gap semiconductor is such that the interband transition is direct, but nominally corresponds to a low-probability, i.e., an almost forbidden optical transition for the CuAu-I-type structure.

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