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Optical method of estimation of degree of atomic ordering within quaternary semiconductor alloys

T. Prutsjij,¹ G. Attolini,² V. Lantratov,³ and N. Kalyuzhnyy³

¹*Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, Privada 17 Norte, No 3417, col. San Miguel Huyeotlipan, 72050 Puebla, Pue., Mexico*

²*Instituto dei Materiali per l'Elettronica ed il Magnetism, CNR, Parco Area delle Scienze 37/A Fontanini, 43010 Parma, Italy*

³*Ioffe Physico-Technical Institute, 26 Polytekhnicheskaya, St Petersburg 194021, Russian Federation*

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It is well known that within metal-organic vapor-phase epitaxy grown semiconductor ternary alloys atomically ordered regions are spontaneously formed during the epitaxial growth. This ordering leads to bandgap reduction and to valence bands splitting, and therefore to anisotropy of the photoluminescence emission polarization. The same phenomenon occurs within quaternary semiconductor alloys. While the ordering in ternary alloys is widely studied, for quaternaries there have been only a few detailed experimental studies of it, probably because of the absence of appropriate methods of its detection. Here, we propose an optical method to reveal atomic ordering within quaternary alloys by measuring the photoluminescence (PL) emission polarization. The measured and calculated angular dependencies of the polarized PL emission intensity from (100) surface for two semiconductor alloys: $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ and $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ are compared in order to estimate the degree of atomic ordering within these alloys. The method shows that the quaternary $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloy is a highly ordered structure with the value of the atomic ordering degree close to 0.5. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4737574>]

I. INTRODUCTION

Intense research performed on $\text{Ga}_x\text{In}_{1-x}\text{P}$ semiconductor alloy over the last decades has shown that the layers of this material obtained by different growth techniques present important differences in their crystalline structure. In particular, it has been experimentally shown^{1,2} that the III group atoms (Ga and In) are not randomly distributed in their crystalline sub-lattice, but rather they present a certain long-, as well as a short-range order. In first studies, the atomic ordering was considered as an undesirable effect for device performance, since epitaxial layers obtained by different techniques have different optical properties and they are not always reproducible. Furthermore, ordering leads to certain inhomogeneities of the crystal itself, since the ordering is never uniform over the layer but only exists in local clusters. It was later realized that a type of ordering, which occurs within the crystal, and the value of the ordering degree could carry information about some peculiarities of atomic arrangement during the growth process, and this effect is exploited to understand different types of inhomogeneities existing within multi-atomic alloys.

Most of the III-V semiconductors crystallize into zinc blende structure that consists of two face-centered-cubic sublattices occupied by atoms of III and V groups. The atomic ordering in ternary alloys occurs within the sublattice containing two different atoms of the same group. In the $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloy, for example, atomically ordered structure consists in a superlattice structure made of alternate Ga-rich and In-rich {111} diagonal planes, with interleaving planes of P atoms, corresponding to CuPt type of ordering.^{1,2} The criterion of the

ordering degree, $0 \leq \eta \leq 1$, is introduced as a value proportional to the increased quantity of one upon another atom of the same group within the alternating Ga- and In-rich monolayers having compositions $\text{Ga}_{x+\eta/2}\text{In}_{1-x-\eta/2}$ and $\text{Ga}_{x-\eta/2}\text{In}_{1-x+\eta/2}$.

The same phenomenon of atomic ordering can occur within III-V quaternary semiconductor alloys.^{3,4} III-V quaternary alloys can be formed by two atoms of group-III and two atoms of group-V, which can be described by the notation $\text{A}_x\text{B}_{1-x}\text{C}_y\text{D}_{1-y}$, where two atoms are in each sublattice; or they can be formed by three atoms of one group and one atom of another group, described as $(\text{A}_x\text{B}_{1-x})_y\text{C}_{1-y}\text{D}$, where three atoms are in the same sublattice. In the first type of quaternary alloys, the atomic ordering can occur within both: III- and V-group sublattices.³ For the second type, the ordering occurs within only the group-III sublattice, as in a ternary alloy.

The disordered alloys have a cubic structure, in which valence bands are degenerated. The ordering leads to the change of the symmetry of the crystal structure and therefore to bandgap reduction and to valence band splitting.^{2,5} Furthermore, as a consequence of the change of the symmetry, the PL emission becomes polarized. A direct method to reveal the ordering is to observe the additional spots in the transmission-electron-diffraction (TED) pattern.⁶ However, the method generally used to estimate the degree of ordering within ternary alloys consists in measuring the reduction of the bandgap energy (with respect to its value in the disordered material) caused by ordering.⁷ This method requires the knowledge of the values of bandgap energies of disordered and fully ordered alloys. The bandgap of a disordered

alloy depends on its atomic composition, and that of a fully ordered alloy is usually determined by calculations. Unfortunately, it is not easy to find out these values for quaternary semiconductors. The atomic content of a disordered quaternary alloy is not defined by the value of the lattice constant (which can be measured by diffractometry), or by its bandgap (measured by PL). For alloys grown on GaAs substrate, for example, a wide range of bandgaps corresponds to the fixed value of the lattice constant given by that of the GaAs. To measure the atomic content of a quaternary alloy, the direct methods, such as energy-dispersive x-ray spectroscopy (EDS) or secondary ion mass spectrometry (SIMS) can be used. These direct methods also can lead to erroneous results because of non-randomness usually observed in quaternary alloys. Besides, no calculations of the bandgaps of fully ordered quaternary alloys were done yet.

Here, we propose an optical method to reveal the atomic ordering within quaternary semiconductor alloys and to estimate its degree by analyzing the angular polarization dependence of its PL emission intensity. In order to show this method, we compare the data measured on the $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ quaternary alloy with the results obtained on the $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ ternary alloy in which the ordering degree was measured independently by the standard and then by this method.

II. GROWTH

The $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ and $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloys were grown on GaAs substrates (001) misoriented 2° towards the [110] direction by low-pressure metal-organic vapor-phase epitaxy (MOVPE). The $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ layer was grown at a temperature of 600°C , and the $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ layer at 725°C in a horizontal reactor with a rotating wafer susceptor. Trimethylaluminum (TMA), trimethylgallium (TMG), and trimethylindium (TMI) were used as group-III sources, and phosphine as group-V precursor. Molar ratio V/III in a gas phase was 80, growth rate was 5 \AA/s and the layer thickness was $\sim 0.6 \mu\text{m}$. A $\sim 300\text{-nm}$ -thick GaAs buffer layer was grown before the $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ layer deposition. After the growth, the surface morphology was examined by scanning electron microscope (SEM), and the atomic content within the layer was measured by SIMS.

III. EXPERIMENTAL PROCEDURE

The polarization angle dependence of the integrated intensity of the PL emission from the surface of the layer was measured using a conventional experimental set-up, which includes a close-cycle He cryostat, a TRIAX550 monochromator, and a liquid-nitrogen-cooled charge-coupled-device (CCD) detector. Optical excitation for PL was provided by an Ar^+ laser (having an excitation wavelength of 514.5 nm). To focus the laser beam to the surface of the sample, the $10\times$ objective was used. To analyze the polarization of the PL emission, a quartz depolarizer and a linear polarizer were installed before the sample, thus the exciting laser beam was depolarized and then linearly polarized before focusing on the sample surface, and then the PL emission was recollimated by the same objective going through the same polarizer and

depolarizer. Therefore, we detected the light polarized along the same direction as the exciting beam. To eliminate the polarization due to the grating, another depolarizer was installed at the entrance slit of the monochromator. The measurements were carried out at low temperature in order to obtain a higher PL intensity. To obtain the integrated PL intensity, the area under the PL peak was calculated by integration of the PL curve.

IV. RESULTS

To show how this method of estimation of the value of atomic ordering degree can be applied to find an ordering within a quaternary alloy, we make a comparison with the data obtained on the ternary $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ alloy, for which the existence of the atomic ordering was established by TEM measurements and the ordering degree was determined using a standard method.

The PL spectra were measured within a wide spectral range in order to achieve two PL emission bands: the peak of the PL emission from the upper $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ or $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ layer, and the peak of the emission from GaAs substrate. As expected, the PL emission of GaAs has less intensity, since more than a half of the excitation intensity is absorbed within the upper layer. To understand the nature of the radiative transitions and to estimate the value of the gap using PL spectra, we measured the spectra of PL emission from these layers within the temperature range of $10\text{--}300 \text{ K}$. These measurements were done without distinction of any polarization. Fig. 1 shows the temperature

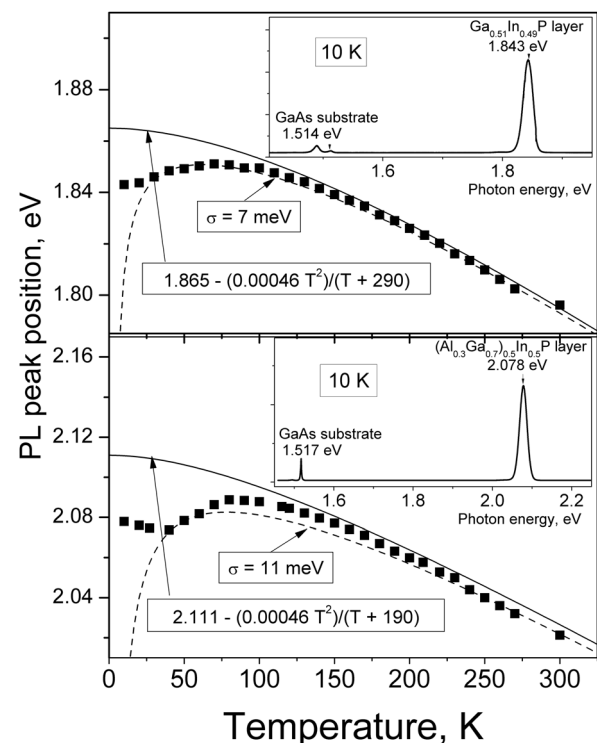


FIG. 1. Temperature behavior of the energy of the PL emission maximum of the $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ and $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloys. The solid lines are the Varshni curves for the set of parameters given in the equation shown below the curve. The dashed lines are the curves obtained considering the energy shift due to the band-tailing effect. PL spectra at low temperature are shown in the inset.

dependencies of the PL peak energy for $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ and $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloys. The insets display the PL spectra measured at low temperature. In the $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ ($(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$) spectrum the higher energy PL band at 1.843 eV (2.078 eV) corresponds to the emission from the upper ternary (quaternary) layer and the low energy band at 1.517 eV, to the emission from GaAs substrate.

The PL spectra of the $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ and the $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloys have only one peak, which can be identified as due to band-to-band transition (E_g). The temperature dependence of its maximum has a S-shape: when the temperature increases, the energy of the PL maximum decreases and reaches a minimum of around 50 K, after this it increases gradually until the temperature reaches approximately 100 K and then begins to decrease akin to the Varshni curve. The S-shaped temperature dependence is commonly found in ordered alloys and can be described by a band-tail model.⁸ It was already mentioned that ordered alloys are never uniform, but consist of ordered clusters within the disordered matrix. Fluctuations of potential created by inhomogeneities produced by ordering are described within this model by a broadening parameter, σ , which characterizes a Gaussian dispersion of a band-tail density of states. Thus, the experimentally obtained temperature dependence of the PL maximum energy can be fitted in terms of the σ^2/kT energy shift, as $E = E_g(T) - \sigma^2/kT$, where $E_g(T)$ is the temperature dependence described by Varshni formula, and k is the Boltzmann constant. The dashed curves in the Fig. 1 correspond to the fit of the measured temperature dependencies using the broadening parameter $\sigma = 7$ meV (11 meV) for the ternary (quaternary) alloy. The higher band-tail induced shift and the corresponding higher value of the broadening parameter are associated with a higher non-randomness within the alloy and in particular to a higher variation of the value of bandgap of ordered clusters, pointing to a higher degree of ordering within the quaternary alloy.

Following the method used in Ref. 9, the optical transition rates for different polarization angles were calculated considering the symmetry of the electronic states at the Γ point and finding the relative values of matrix elements for the optical transitions from the conduction band to each one of split valence bands for the Cu-Pt type of ordering. Then, assuming parabolic bands and Boltzmann statistics, the emission intensity ratio, I_θ , as a function of the polarization angle θ was calculated. In order to compare the calculated PL rate with the measured PL intensity, the contribution of all polarizations to the PL intensity for a given polarizer direction, φ , was considered by integrating the emission rate to obtain:
$$I(\varphi) = \frac{1}{2\pi} \int_{-\pi}^{\pi} I_\theta \cos^2(\theta - \varphi) \cdot d\theta.$$

The measured and calculated angular polarization dependencies of the intensity of the PL emission from the (001) surface of the $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ layer are compared in Fig. 2. The ordering degree for this layer, used in the calculation, was obtained from the value of the band gap reduction due to the ordering. We measured the PL emission maximum at room temperature (1.80 eV) that corresponds to the energy of the band-to-band transitions, i.e., to the value of the bandgap. The In content in the layer, 0.49, was measured using the SIMS technique. For a disordered alloy with this In

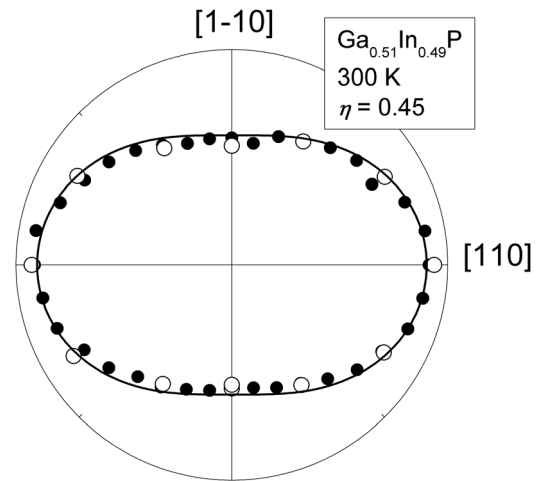


FIG. 2. Measured and calculated angular dependencies of the PL integrated intensity of the emission from $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ alloy and the comparison of the data obtained using different setups. Empty circles correspond to measurements performed using the polarization of the excitation laser beam along [110] direction. Full circles correspond to the measurements in which the measured PL emission polarization is the same as that of the laser beam. The line corresponds to the angular dependence calculated using the value of the ordering degree $\eta = 0.45$.

content, the value of the band gap would be 1.90 eV. Thus, following the criterion of Ref. 7, the ordering parameter $\eta = 0.45$ was found.

In the same Fig. 2, we compare the angular polarization dependencies measured using different setups. It must be pointed out that the intensity of the PL emission polarized along the same direction as that of the exciting laser beam is measured using the experimental setup described in Sec. III. In order to be certain that the measured PL emission intensity does not depend on the exciting beam polarization, we compare the angular dependence measured using this setup with that measured using the excitation laser beam polarized along the [110] crystalline direction. A comparison of the angular polarization dependencies of the PL intensities measured with different polarizations of exciting beam shows that there is no significant difference between them.

The PL spectra of the $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloy corresponding to two orthogonal polarizations are shown in Fig. 3(a). The different values of integral intensity of the peaks of PL emission from $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ layer observed for two orthogonal polarization directions evidence that the PL emission is anisotropic. However, PL measurements performed for only two polarization directions, are not enough to estimate the value of the ordering degree, and the angular dependence of the PL intensity has to be considered. The measured and calculated angular dependencies of the integrated PL intensity with the polarization angle of the $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloy are shown in Fig. 3(b). Each point of the measured dependence of the PL intensity corresponds to the intensity of the PL emission polarized along that direction. The solid line corresponds to the calculated rate of radiative transitions for each polarization direction using the value of the ordering parameter, η , which provides a better fit to the experimental curve. As one can see, the angular dependence of the PL intensity points out that the $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloy is strongly ordered having the

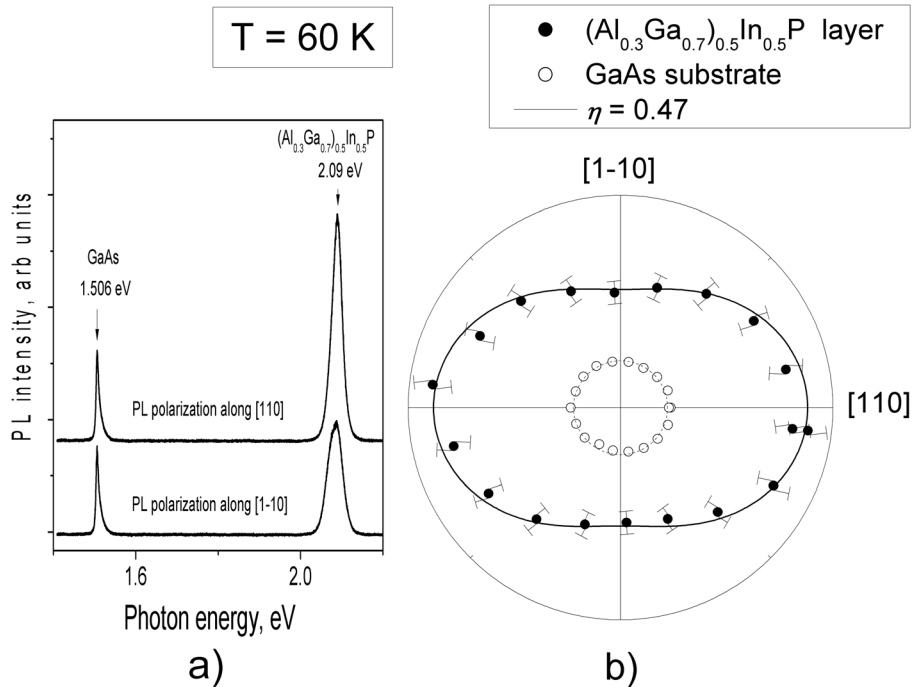


FIG. 3. (a) PL emission spectra of the $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloy for two orthogonal polarizations, (b) polar plot of the PL intensity versus the polarization angle for the $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloy (full circles), and for GaAs substrate (empty circles). The solid line corresponds to the PL integrated intensity calculated using the value of the ordering degree $\eta = 0.47$.

ordering parameter of 0.47. (Using the fitting procedure we estimate the uncertainty of this value to be approximately 0.08.) This value is close to 0.5, predicted in Ref. 10 as a value of the maximum ordering degree that could be reached within $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloy. The greater value of the ordering parameter of the quaternary alloy is consistent with the greater broadening parameter, σ , found by analyzing the temperature evolution of its bandgap.

The degree of anisotropy of the PL emission polarization depends also on the values of several parameters of the ordered alloy such as the values of electron and hole effective masses and the value of valence band splitting for the completely ordered alloy, which for the $\text{Al}_x\text{Ga}_{1-x}\text{In}_y\text{P}$ alloy are not available. However, it can be seen from the fitting procedure that these values change greatly the rate of radiative transitions and do not modify significantly the angular polarization dependence; therefore the parameters of the $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloy were used for calculations. Considering that within the $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ ordered alloy Al/Ga rich (111) planes alternate with In-rich planes, and, because of the fact that Al and Ga have a very similar covalent radii, close values of the effective masses can be expected for this alloy. Taking into account also that the atomic content of Al in the $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.5}\text{In}_{0.5}\text{P}$ alloy is relatively small, we assume that the value of valence band splitting of the fully ordered $\text{Ga}_{0.5}\text{In}_{0.49}\text{P}$ alloy can be used for the quaternary alloy to calculate the angular dependence of the integrated PL intensity with the polarization angle.

In Fig. 3(b), the angular dependence of the PL intensity of the emission from GaAs substrate is also shown. As one can see, the PL emission of GaAs is not polarized. Since the

polarization of the PL emission is the consequence of the atomic ordering and no ordering can occur in binary compounds, the fact that no polarization of the PL emission from the substrate was found, verifies that the experiment was carried out properly.

In summary, we showed that the angular polarization dependence of the PL intensity can be used to reveal the presence of atomic ordering within quaternary alloys and the comparison with the PL intensity calculated curves allows to estimate its degree.

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