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Optical properties of ordered $In_{0.5}Ga_{0.5}P$ alloys

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We study the structural stability and the optical properties of ordered $In_{0.5}Ga_{0.5}P$ alloys in the CuPt-, CuAu-I-, and Y2-type structures through first-principles pseudopotential calculations. The Y2-type structure is found to be stabilized against phase segregation into binary constituents at $T=0$ when epitaxially grown, with the smaller formation enthalpy than for the CuPt- and CuAu-I-type phases. The CuPt- and Y2-type structures show an asymmetry feature in $\epsilon_2(\omega)$ for two perpendicular polarizations along the [110] and $[1\bar{1}0]$ directions. We find that in the CuPt-type structure the zone folding effect of the L point into the center of the Brillouin zone leads to the enhancement of $\epsilon_2(\omega)$, giving rise to an anomalous peak at 2.35 eV in electroreflectance spectra, while the lower energy peak observed at 2.2 eV is caused by the folded-X point in the Y2-type structure.

Recently, $In_{0.5}Ga_{0.5}P$ alloys have attracted much attention in both scientific and technological aspects, and these materials have potential applications for optical and optoelectronic devices, such as laser diodes[1,2] and solar cells.[3] In samples grown by metal-organic vapor phase epitaxy (MOVPE), an ordering in the epitaxial layers has been found, which is mostly assigned as the CuPt-type ordering along the [111] direction.[4–12] One of interesting features in the ordered alloys is the variation of the optical band gap by about 100 meV depending on growing conditions such as growing temperature and III/V mole ratio.[4–10] The band-gap variation was explained in terms of the folding of the L point in the Brillouin zone induced by the [111] ordering.[13] Ordered $In_{0.5}Ga_{0.5}P$ alloys exhibit anomalous optical peaks in electroreflectance[2,6–8] and photoreflectance spectra,[2] a variable Raman line shape,[5,6] and a shift in low-temperature photoluminescence (PL).[9,10] Since the spontaneous ordering is not perfectly distributed over the epitaxial layer, other orderings may coexist with the dominant CuPt-type structure in MOVPE-grown samples. Electroreflectance spectroscopy showed anomalous peaks at about 2.2 and 2.35 eV, which lie above the E_0 energy. Kurtz[14] attributed the 2.2-eV peak to the X point zone folding due to the Y2-type ordering along the [001] direction and the 2.35-eV peak to the L point zone folding due to the CuPt-type [111] ordering. The PL spectra of $In_{0.5}Ga_{0.5}P$ under pressure supported the existence of such an [001] ordering.[15]

In this work, we investigate the structural stability and the optical properties of the ordered $In_{0.5}Ga_{0.5}P$ semiconducting alloys in the CuPt-, CuAu-I-, and Y2-type structures through the first-principles pseudopotential calculations. We find that the formation enthalpy of the Y2-type structure is smaller than those for the CuPt- and CuAu-I-type phases. For epitaxially grown samples, the Y2-type structure is stabilized against phase segregation into binary constituents with a negative formation enthalpy. To study the optical properties, we calculate the imaginary part of the dielectric function, $\epsilon_2(\omega)$, for each structure. The anisotropy of the dielectric response function is investigated by changing the polarization direction of an external field. An asymmetric feature in $\epsilon_2(\omega)$ is found for the CuPt- and Y2-type structures. In the CuPt-type superlattice, we find that the zone folding effect of the L point leads to the enhancement of $\epsilon_2(\omega)$, which gives rise to the anomalous peak observed at 2.35 eV, consistent with previous studies. For the Y2-type ordered phase, we suggest that the absorption peak at 2.2 eV is mainly caused by the optical transitions to the folded-X point in the Brillouin zone.

Our calculations are based on the first-principles pseudopotential method[16,17] within the local-density-functional approximation (LDA).[18] The Wigner interpolation formula[19] is used for the exchange and correlation potential. Norm-conserving semilocal pseudopotentials are generated by the scheme of Troullier and Martins[20] and transformed into the separable form of Kleinman and Bylander.[21] The wave function is expanded in a plane-wave basis set with a kinetic energy cutoff of 15 Ry throughout this work, thus, sufficient convergence for the band structure is achieved. To calculate the formation enthalpy for each structure, we use the set of **k** points which is equivalent to the Chadi's ten special points[22] to ensure consistency in comparison of the total energies between the ordered superlattices and pure binary compounds.

We consider three types of ordered structure to investigate the stability and the optical properties of $In_{0.5}Ga_{0.5}P$ alloys, which are drawn in Fig. 1. The CuPt- and CuAu-I-type structures have a long-range order along the [111] and [001] directions, respectively, with alternate stackings of monolayer InP and GaP along the ordering direction. In the CuPt-type structure, the L point in the zinc-blende Brillouin zone (BZ) is folded into the center. In the CuAu-I-type structure, the zone folding effect brings the X point lying in the [001] superlattice direction to the center of the superlattice BZ while it leaves the X points on the superlattice plane unchanged. Although the Y2-type structure has an identical basal plane to that of the CuPt-type structure, as shown in Fig. 1, the same planes are repeated at every zinc-blende cubic cell along the [001] direction in this structure. Since the Y2-type phase is actually a two-layer superlattice $(InP)_2/(GaP)_2$ along the [110] direction, both the Σ and X points are folded into the center of the superlattice BZ.

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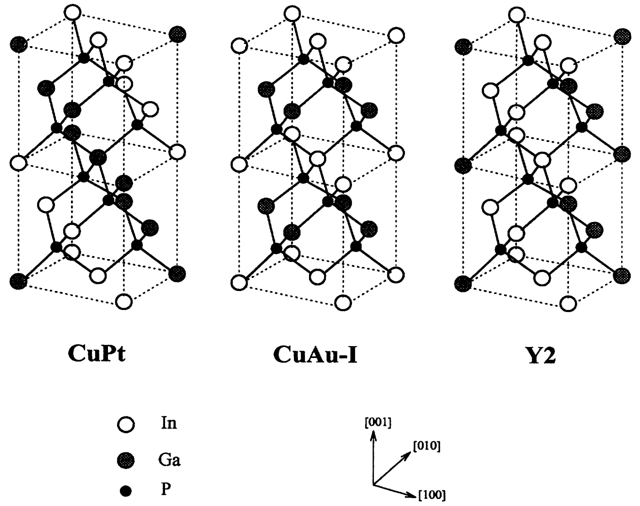

FIG. 1. Atomic structures for the CuPt-, CuAu-I-, and Y2-type $\mathrm{In_{0.5}Ga_{0.5}P}$ superlattices.

To examine the structural stability of an $\mathrm{In_{0.5}Ga_{0.5}P}$ superlattice in structure α with respect to phase segregation into binary constituents, we calculate the bulk formation enthalpy $\Delta H_{\mathrm{bulk}}^{(\alpha)}$ and the epitaxial one $\Delta H_{\mathrm{epi}}^{(\alpha)}$ per anion-cation pair at $T=0$, defined as

$$\Delta H_{\mathrm{bulk}}^{(\alpha)}(\mathrm{In_{0.5}Ga_{0.5}P}) = E^{(\alpha)}(\mathrm{In_{0.5}Ga_{0.5}P}) - [E^{(0)}(\mathrm{InP}) + E^{(0)}(\mathrm{GaP})]/2, \tag{1}$$

$$\Delta H_{\mathrm{epi}}^{(\alpha)}(\mathrm{In_{0.5}Ga_{0.5}P}) = E_{\mathrm{epi}}^{(\alpha)}(\mathrm{In_{0.5}Ga_{0.5}P}, a_{\parallel}=a_s) - [E_{\mathrm{epi}}(\mathrm{InP}, a_{\parallel}=a_s) + E_{\mathrm{epi}}(\mathrm{GaP}, a_{\parallel}=a_s)]/2, \tag{2}$$

where $E^{(\alpha)}(\mathrm{In_{0.5}Ga_{0.5}P})$, $E^{(0)}(\mathrm{InP})$, and $E^{(0)}(\mathrm{GaP})$ are the energies for $\mathrm{In_{0.5}Ga_{0.5}P}$, InP, and GaP, respectively, in their equilibrium bulk structures. In epitaxial forms, we imagine thin pseudomorphic strained superlattices grown on (001) GaAs, with the in-plane lattice constant $a_{\parallel}$ fixed at the epitaxially confined value a_s on the substrate. The results for ΔH_{bulk} and ΔH_{epi} are listed in Table I and good agreements with previous calculations are found for the CuPt- and CuAu-I-type structures.[23,24] Small discrepancies between the two calculations result from the use of different *ab initio* pseudopotentials. It is found that the CuAu-I-type structure is more stable than the CuPt-type structure. However, both the CuPt- and CuAu-I-type structures in epitaxial forms are unstable against phase segregation into binary constituents, thus, the observed $[\bar{1}11]$- or $[1\bar{1}1]$-ordered $\mathrm{In_{0.5}Ga_{0.5}P}$ was suggested to be related to chemical-bonding effects at the growing surface.[23,25] For both bulk and epitaxial superlattices in the Y2-type structure, their formation enthalpies are found to be smaller than those for the CuPt- and CuAu-I-type structures, and the epitaxial form is stabilized against phase segregation with a negative formation enthalpy. Although the CuPt-type ordering was dominantly observed, there are some indications for the existence of the Y2-type structure.[14,15]

The optical properties of $\mathrm{In_{0.5}Ga_{0.5}P}$ superlattices are examined by calculating the imaginary part of the dielectric function, $\epsilon_2(\omega)$. In the optical limit $\mathbf{q}\rightarrow 0$, $\epsilon_2(\omega)$ provides information on the absorption spectrum and is expressed in terms of the band structure and the dipole matrix elements:

$$\epsilon_2(\omega) = \frac{4\pi^2}{\omega^2} \sum_{v,c} \int \frac{2d\mathbf{k}}{(2\pi)^3} |\langle c,\mathbf{k}|\mathbf{e}\cdot\mathbf{p}|v,\mathbf{k}\rangle|^2 \times \delta(\varepsilon_{c,\mathbf{k}} - \varepsilon_{v,\mathbf{k}} - \omega), \tag{3}$$

where $|c(v),\mathbf{k}\rangle$ and $\varepsilon_{c(v),\mathbf{k}}$ are the wave function and the energy eigenvalue, respectively, for the conduction (valence) band state at a $\mathbf{k}$ point, $\mathbf{e}$ is the polarization vector of an external field, and $\mathbf{p}$ is the momentum operator. Since the contributions to the matrix elements from the nonlocal pseudopotentials are known to be small in the limit $\mathbf{q}\rightarrow\mathbf{0}$, these terms are neglected in our calculations. To perform the summation over the Brillouin zone, the linear tetrahedron method is employed.[26,27] If we use the unit cells containing 4, 4, and 8 atoms for the CuPt-, CuAu-I-, and Y2-type structures, respectively, the irreducible sector of the Brillouin zone for each structure has a rather complicated shape, thus, the division of the irreducible sector into a set of small tetrahedrons becomes a complex matter. To avoid this problem, we perform the integration in Eq. (3) over the full Brillouin zone. Considering the symmetry operations, we further reduce computational efforts by choosing a minimum number of $\mathbf{k}$ points at which the single-particle eigenvalues and wave functions are calculated. For the CuPt-, CuAu-I-, and Y2-type structures, we use 6615, 4851, and 3465 $\mathbf{k}$ points, respectively, in the full Brillouin zone and include 22, 22, and 34 conduction band states, respectively, in the band summation to ensure calculational accuracy in the energy range of our interest.

The densities of states for ordered $\mathrm{In_{0.5}Ga_{0.5}P}$ superlattices in the CuPt-, CuAu-I-, and Y2-type structures are shown and compared in Fig. 2. For all the structures, the direct band

TABLE I. The bulk (ΔH_{bulk}) and epitaxial formation enthalpies (ΔH_{epi}) are compared for ordered $\mathrm{In_{0.5}Ga_{0.5}P}$ alloys in the CuPt-, CuAu-I-, and Y2-type structures. The (001) surface of GaAs is used as a substrate for epitaxially grown samples.

	Present calculations			Other calculations	
Structure	CuPt	CuAu-I	Y2	CuPt	CuAu-I
ΔH_{bulk} (meV/atom)	34.0	26.8	15.3	30.5,[a]33.8[b]	21.3,[a]22.8[b]
ΔH_{epi} (meV/atom)	10.8	2.4	−6.3	11.7[a]	4.6[a]

[a] Reference 23.

[b] Reference 24.

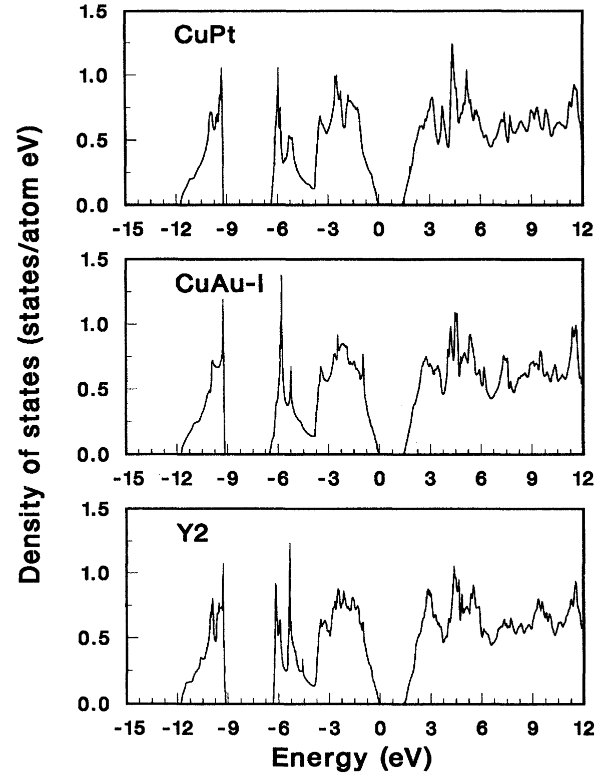

FIG. 2. The densities of states for the CuPt-, CuAu-I-, and Y2-type structures are drawn. For each structure, the valence-band maximum is chosen as reference.

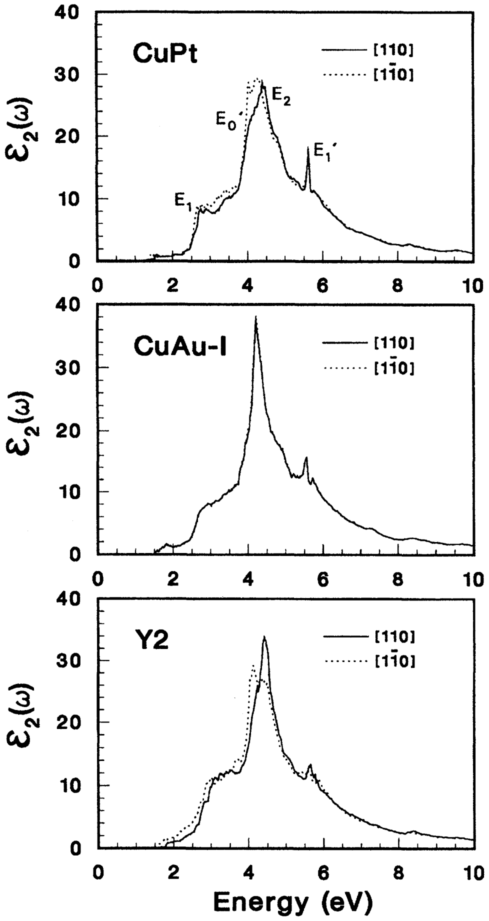

FIG. 3. The imaginary parts of the dielectric functions for the [110] and [1$\bar{1}$0] (dotted) polarizations are plotted for $In_{0.5}Ga_{0.5}P$ alloys in the CuPt-, CuAu-I-, and Y2-type structures.

gaps are found at the Γ point, with the smallest band gap of 1.10 eV for the CuPt-type structure, while their values are 1.27 and 1.28 eV for the CuAu-I- and Y2-type phases, respectively. It was shown that the small band gap in the CuPt-type structure results from the zone folding and band repulsion effects.[13] The densities of states in the valence band are slightly different from those for binary compounds, InP and GaP. The peak at about -6 eV split into several peaks, and the Y2-type structure which has the largest unit cell shows the most different feature from those for the binary compounds.

The imaginary part of the dielectric function is plotted for the [110] and [1$\bar{1}$0] polarizations in Fig. 3, which are perpendicular to the [001] epitaxial growing axis. For both the CuPt- and Y2-type superlattices, since the projections of two polarization vectors onto the ordering direction differ from each other, these structures show an asymmetric feature in $\epsilon_2(\omega)$, while it is symmetric for the CuAu-I-type phase. All the structures considered here exhibit the E_1, E_0', E_2, and E_1' peaks, which characterize the absorption spectra of zinc-blende InP and GaP.[28] In the binary compounds, the E_1 and E_0' peaks are originated from interband transitions near the L and Γ points in the BZ, respectively. The E_2 peak which dominates the absorption spectra arises from optical transitions from the valence band maximum (VBM) states to the conduction band minimum (CBM) states near the special point, $(3/4,1/4,1/4)(2\pi/a)$, while the E_1' peak is associated with interband transitions from the VBM states to the second CBM states near the L point.

In the ordered superlattices, the heights of the E_1 peaks are much reduced, as compared to bulk InP and GaP. Since the Y2-type structure has many valence states close to the VBM near the L point, the E_1 peak exhibits rich structures. For the [110] and [1$\bar{1}$0] polarizations, we find the absorption spectra in the CuPt- and Y2-type structures to be anisotropic, particularly, at the E_2 peak, while it is isotropic in the CuAu-I-type structure. In the CuAu-I-type structure, both the [110] and [1$\bar{1}$0] layers consist of either InP or GaP, as shown in Fig. 1. Since the stacking sequences of these InP and GaP layers are the same along the [110] and [1$\bar{1}$0] polarization directions, the CuAu-I-type structure has an isotropic feature in $\epsilon_2(\omega)$ with the sharpest E_2 peak, similar to those for the binary compounds. In the Y2-type structure, the absorption spectra for the [1$\bar{1}$0] polarization is slightly shifted to lower energies, as compared to the [110] polarization. This ordered superlattice has pure InP and GaP layers stacked along the [110] direction, thus, a similar sharp E_2 peak appears for the [110] polarization. However, since the In and Ga atoms are mixed in each [1$\bar{1}$0] layer, the E_2 peak for the [1$\bar{1}$0] polarization is splitted and broadened. In the CuPt-type superlattice, both the [110] and $[1\bar{1}0]$ planes are mixed with the In and Ga atoms, thus, the anisotropy of $\epsilon_2(\omega)$ is prominent. In this case, since the [111] ordering direction along which monolayers InP and GaP are alternately stacked is perpendicular to the $[1\bar{1}0]$ polarization while it is oblique to the [110] polarization axis, the broadening of the E_2 peak is more significant for the $[1\bar{1}0]$ polarization. Similar splittings by anisotropic crystal fields were also found in hexagonal semiconductors, such as CdS, CdSe, and ZnS,[29] where the dominant absorption peak E_1 splits into two peaks for polarizations perpendicular to the hexagonal axis. In this case, when the crystal structure changes from the zinc-blende to the wurtzite structure, two of the eight equivalent [111] directions are mapped into the high-symmetry Γ-A axis of the hexagonal BZ and cause the broadening of the peak, while the other six [111] directions go into points of lower symmetry, resulting in the major peak. Similarly, the **k** points near the $(3/4,1/4,1/4)(2\pi/a)$ point of the zinc-blende BZ, which are responsible for the E_2 peak in binary compounds, InP and GaP, may be divided into higher and lower symmetry regions in the superlattice BZ. Then, because of the different selection rules for optical transitions at points of high and low symmetries, a splitting of the E_2 peak occurs. Regarding the E_1' peak, we find that the VBM and second CBM states along the unfolded Γ-L direction are nearly parallel in the CuPt-type structure, leading to the sharpest peak.

Figure 4 shows the details of the absorption spectra near the band gap energy for the [110] polarization. In the CuPt-type structure, we find rapidly increasing behavior at about 1.5 and 2.0 eV. Such a large enhancement of $\epsilon_2(\omega)$ at about 1.5 eV may arise from interband transitions between the VBM and CBM states over a wide range of the Brillouin zone, although an exact assignment is difficult at this point. In this phase, because of the band repulsion effect, the average separation of about 1.8 eV between the highest occupied and lowest unoccupied states along the folded Γ-L direction is found to be reduced by about 0.2 eV, as shown in Fig. 5, compared with the unfolded Γ-L axis. The rapid increase at 2.0 eV originates from the transition from the VBM to the folded-L state at the Γ point, denoted by A in Figs. 4 and 5, which is assigned as the 2.35-eV peak among two anomalous peaks observed in the electroreflectance spectra.[2,6–8] This peak was also suggested to result from the folding effect of the L point into the center of the superlattice BZ.[14] The discrepancy between the calculated and measured positions for this peak is attributed to the incorrect description of the conduction bands by the LDA. The origin of the lower energy peak at about 2.2 eV in the electroreflectance spectra is less well defined, as compared to the 2.35-eV peak. Kurtz suggested that this peak is caused by the band folding of the X point due to the [001] ordering in the Y2-type structure. Uchida and his co-workers[15] examined the PL spectra for MOVPE-grown InGaP samples under pressure. From the pressure behavior of the conduction band states, they concluded that the 2.2-eV peak is explainable in terms of the superlattice ordering along the [001] direction.

In the CuAu-I- and Y2-type structures, the second CBM states at the Γ point are derived from the X point due to the band-folding effect, and their positions are found to be higher by about 0.24 and 0.08 eV, respectively, than the CBM state, as shown in Fig. 5. On the other hand, the second VBM states at the Γ point lie at about 0.10 and 0.15 eV, respectively, below the VBM state. Because both the CuAu-I- and Y2-type structures have the [001] ordering, these structures may contribute to the anomalous peak observed at 2.2 eV in the electroreflectance spectra. To investigate the origin of the 2.2 eV peak, we calculate oscillator strengths for various interband transitions at the Γ point, and the results are listed in Table II. We find that interband tran-

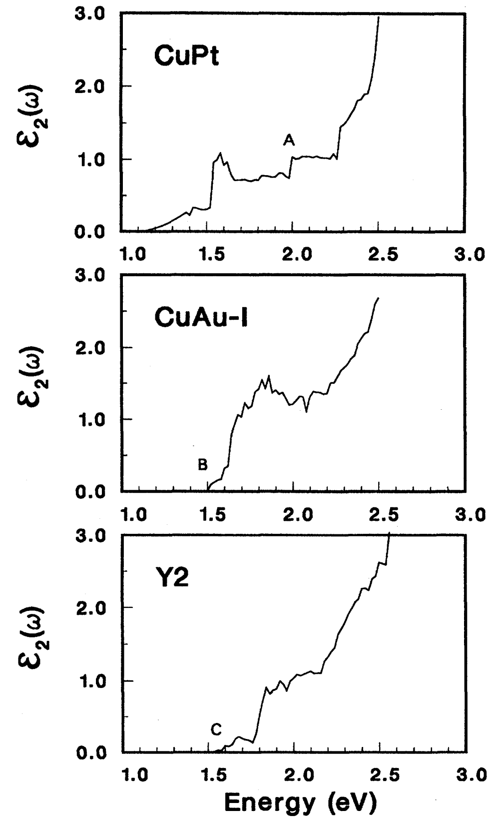

FIG. 4. Large views of $\epsilon_2(\omega)$ near the band gap energy for the [110] polarization.

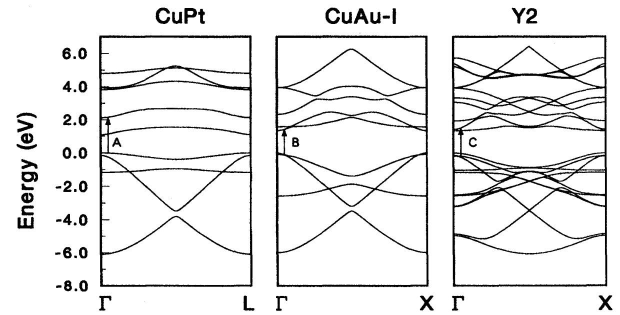

FIG. 5. The band structures for the CuPt-, CuAu-I-, and Y2-type $\mathrm{In}_{0.5}\mathrm{Ga}_{0.5}\mathrm{P}$ superlattices are plotted along the folded symmetry lines in the superlattice Brillouin zone. The arrows denote interband transitions responsible for the optical peaks shown in Fig. 4.

TABLE II. The oscillator strengths (f_{cv}) for interband transitions from the valence band to the conduction band states are listed. Energy separations are given by ΔE in units of eV and band orderings are denoted by i in $\Gamma_{iv(c)}$, which indicates the ith valence (conduction) band state from the valence (conduction) band maximum (minimum).

	CuAu-I		Y2	
Transitions	ΔE	f_{cv}	ΔE	f_{cv}
$\Gamma_{3v}\rightarrow\Gamma_{1c}$	1.37	11.08	1.46	9.55
$\Gamma_{3v}\rightarrow\Gamma_{2c}$	1.61	0.01	1.54	48.33
$\Gamma_{2v}\rightarrow\Gamma_{1c}$	1.37	4.83	1.43	3.39
$\Gamma_{2v}\rightarrow\Gamma_{2c}$	1.61	0.00	1.51	15.67
$\Gamma_{1v}\rightarrow\Gamma_{1c}$	1.27	0.00	1.28	0.00
$\Gamma_{1v}\rightarrow\Gamma_{2c}$	1.51	0.00	1.36	0.00

sitions from the VBM state to the CBM and second CBM states are forbidden in both the CuAu-I- and Y2-type structures. Although the optical transitions from the second VBM state to the CBM state are allowed, their oscillator strengths are found be very small. In the CuAu-I-type structure, the oscillator strengths for the transitions to the folded-X state are negligible, and the optical transitions to the CBM state give rise to the absorption edge B in Fig. 4. However, the Y2-type structure shows substantial oscillator strengths for the transitions (denoted by the arrow C in Fig. 5) from the second and third VBM states to the folded-X point, which are responsible for the absorption edge C at about 1.5 eV in Fig. 4. The energy separation of 0.4 eV between the absorption edge C and the fundamental band gap of the CuPt-type structure is similar to the measured difference of 0.35 eV between the 2.2-eV peak and the band gap in MOVPE-grown samples. Furthermore, the absorption edge C is led by interband transitions to the folded-X state, thus, we suggest that the Y2-type structure is responsible for the anomalous 2.2-eV peak.

In conclusion we have studied the structural stability and the optical properties of ordered $In_{0.5}Ga_{0.5}P$ alloys. We find that the Y2-type structure is more stable than the CuPt- and Y2-type ordered superlattices, with a negative formation enthalpy when grown epitaxially on (001) GaAs. For the [001] and [$1\bar{1}0$] polarizations, both the CuPt- and Y2-type structures exhibit an asymmetric feature in $\epsilon_2(\omega)$, while the absorption spectra are symmetric for the CuAu-I-type structure. In the CuPt-type structure, the band-folding effect of the L point into the center of the superlattice Brillouin zone leads to the enhancement of the optical absorption, which is attributed to the 2.35-eV peak observed in the electroreflectance spectra. We suggest that the other optical peak at 2.2 eV is associated with interband transitions to the folded-X point in the Y2-type structure, and the Y2-type ordering coexists with the dominant CuPt-type ordering in $In_{0.5}Ga_{0.5}P$ alloys.

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