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Observation of a martensitic transition in the Raman spectra of ordered GaInP

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Abstract. We have observed a strong dependence of the intensity of the ordering-induced phonon bands on thermal treatment (rapid cooling and annealing) in Raman spectra (RS) of CuPt_B ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloys. The changes of the Raman intensity occur only in diagonal backscattering configuration: $y' \parallel [\bar{1}10]$, where the polarization of light is parallel to the mirror planes of the ordered structure. We found that there are at least two different intensity distributions of the optical phonon bands the appearance of which is determined by thermal treatment and the alloy film thickness. The bond polarizability model analysis shows that the observed RS behaviour can be described in terms of the order-disorder martensitic transition on trigonal lattice sites.

1 Introduction

It is well known that microstructure of nearly all technologically important semiconductor alloys exhibit strong deviations from random atomic distribution [1]. These deviatioons appear as phase separation, short- and long-range order effects and are determined by thermodynamics and kinetics of the growth process. When the distribution of the atoms in alloy lattice sites is fixed, there exists degrees of freedom associated with crystal lattice-site rearrangement. The phase transformation in the alloys that can be treated only in terms of the displacements is known in classical metallurgy as diffusionless (martensitic) transformation [2]. Here we present results of the first observation of the martensitic transformation in epitaxial films of a semiconductor alloy. The alloy system is a CuPt_B-type long range ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloy [1], and the transition is revealed as a strong change of the Raman intensity of optical phonon modes on rapid cooling of the alloy. A bond polarizability model analysis shows the connection of the Raman intensities of the long-range ordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ with trigonal lattice site rearrangement.

2 Experiment

Samples used were grown by MOVPE at temperature about 650 °C on (001) GaAs substrates. A substrate orientation of 6° miscut towards the $[111]_\text{B}$ direction was used to obtain a single orientation of the ordered CuPt_B-type structure ($[111]_\text{B}$-GaP/InP monolayer superlattice). We have investigated two samples with ordering degree about 0.5 and epilayer thickness 0.3 (“thin”) and 3 μm (“thick”). The thermal treatment consisted of a rapid cooling down to 77 K, followed by annealing at $T = 400°\text{C}$ for 30 minutes. After each treatment the backscattering Raman spectra (RS) were measured at 300 K in the $x'x'$ and $y'y'$ configurations, where $x' \parallel [110]$ and $y' \parallel [\bar{1}10]$. The intensities of the Raman bands were analysed using Lorentzian contour modeling [3, 4]. Lattice dynamical calculations of the perfectly ordered GaInP_2 CuPt_B structure was performed using the Valence Overlap Shell model (VOSM).

3 Raman selection rules for perfectly ordered GaInP$_2$ CuPt$_B$ structure

We used the bond polarizability model (BPM) [5, 6] for deriving selection rules for optical phonons of the GaInP$_2$ CuPt$_B$ structure. The BPM unit of this structure consists of two trigonal In$_3$GaP and Ga$_3$InP tetrahedrons (eight non-equivalent bonds). Using approach described in [6] and assuming zinc-blende bond angles, a structure-dependent part of its Raman tensor can be written as follows:

$$\tilde{R}^Z = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2(1-\Delta^\nu) \end{bmatrix} \tilde{R}^Y = \begin{bmatrix} -\sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & -1 \\ 0 & -1 & 0 \end{bmatrix} \tilde{R}^X = \begin{bmatrix} 0 & \sqrt{2} & -1 \\ \sqrt{2} & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix}$$

Here the term Δ reflects a trigonal distortion of the Raman polarizability of the zinc-blende lattice. In an assumption, that the bond polarizability is equal for four bonds of one sort (In-P and Ga-P), Δ depends only on phonon eigenvectors. The strong localization of GaP and InP-type phonons in the corresponding monolayers, found in the lattice dynamical calculations, allows to write $\Delta = (9/8)(1 - \Delta u_z)$, where $\Delta u_z = u_z^{\mathrm{PI}} / u_z^{\mathrm{PII}}$ is the ratio of the Z component of the displacements of two basis P atoms.

For only the R^Z_{zz} component contains the trigonal contribution, only the Raman configurations having Z components of an incident and scattered electric field will be sensitive to it. In Table 1 we presented the corresponding selection rules for phonons with pure LO and TO polarizations. It is seen from Table 1, that only the $y'y'$ configuration includes Δ contribution. The TO phonons are allowed only in the $y'y'$ configuration and only for nonzero values of Δ. Thus they can be activated in alloy only in the presence of CuPt$_B$ long-range order. These selection rules can fully explain the $\{110\}$-anizotropy of diagonal components observed in Raman spectra of spontaneously ordered Ga$_{0.5}$In$_{0.5}$P alloys [4] and make an assignment of the ordering induced bands (see further discussion).

Table 1. Raman selection rules for the $\Gamma^{\sigma 211}$ phonons.

Scattering geometry	Scattering intensity LO	Scattering intensity TO
$z(x'x')z$	1	0
$z(y'y')z$	$(1-4/9\Delta)^2$	$32/82\Delta^2$

4 Raman spectra of thermally treated alloy and discussion

The experimental RS of thermally treated "thick" sample are presented in Fig. 1(a-c). Here the subscripts 1 and 2 are used for GaP and InP type vibrations and additional subscript e is used for the ordering-induced phonons.

The assignment of the ordering induced bands in Fig. 1(a) (initial state of the sample) was done using difference of the bands intensity in $x'x'$ and $y'y'$ configurations, rules from Table 1 and the results of the lattice dynamical calculations (see Table 2). The $\{110\}$ intensity anisotropy of the LO$_{1e}$ and LO$_{2e}$ phonons was derived from the Lorentzian modeling. The appearance of the pure $y'y'$ line TO$_{1e}$ at 351 cm^{-1} in Fig. 1(a), is well predicted from our calculations.

The spectra in Fig. 1(b) show that $x'x'/y'y'$ intensity anisortopy have significant changes after rapid cooling. The changes appear as a strong decrease of the intensity

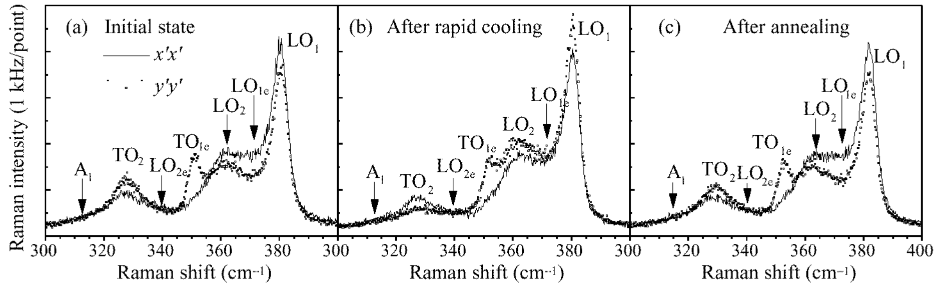

Fig 1. Raman spectra of the “thick” sample after different stages of thermal treatment: (a) initial state, (b) after rapid cooling, (c) after annealing. The spectra were measured in the backscattering $x'x'$ (solid curves) and $y'y'$ (dotted curves) configurations.

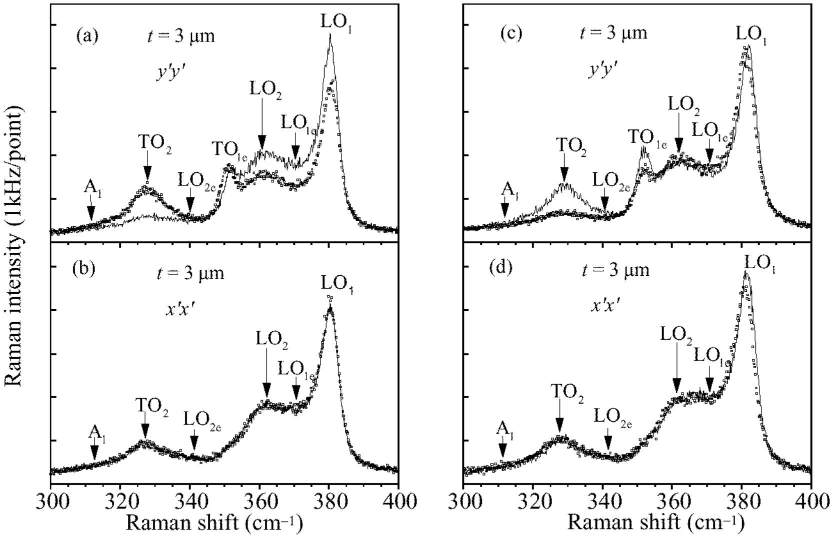

Fig 2. Thermal treatment dependence of the $y'y'$ (a, c) and $x'x'$ (b, d) RS of the “thick” and “thin” samples. Dotted curves: initial state, solid curves: after cooling.

of the TO_{1e} and TO_2 bands and increasing of the intensity of the LO_1, LO_{1e}, LO_2 and LO_{2e} bands in $y'y'$ configuration (see Fig. 2a,b). In Fig. 2(c-d) we also present $x'x'$ and $y'y'$ spectra for the thermally treated “thin” sample. One can see that the RS spectra of both samples are very similar, except the unusual fact that the intensity distribution of the bands in RS of the “thin” sample in its initial state is similar to the intensities of the “thick” sample after cooling, and spectra of the “thick” sample before cooling are similar to the “thin” sample after cooling. We have found, that annealing restores the initial band intensities (Fig. 1c). This can also be achieved by “annealing” the sample at room temperature for several weeks.

It is natural to connect the observed changes in the Raman band intensities with the changes of equilibrium atom positions, i.e. lattice state vector. Therefore, changing in the RS after thermal treatment is direct evidence of the martensitic transition in spontaneously ordered $Ga_{0.5}In_{0.5}P$. The difference in RS of the “thick” and “thin” samples shows, that a spontaneously ordered $Ga_{0.5}In_{0.5}P$ alloy film has at least two equilibrium

Table 2. Frequencies (cm^{-1}) of the $\mathrm{GaInP_2}$ CuPt structure optical phonons, measured from Raman spectra and calculated using VOSM.

Mode type	$\mathrm{TO_{o2}}$	$\mathrm{TO_{e2}}$	$\mathrm{LO_{e2}}$	$\mathrm{TO_{e1}}$	$\mathrm{TO_{o1}}$	$\mathrm{LO_{e1}}$
Calculation	324.4	327.8	342.3	355.1	360.3	381.5
Experiment	—	328	340	351	—	370

lattice states, the energetic preference of which is determined by the elastic strain between the film and the substrate. In RS the difference between these two states appears as the difference in the $x'x'/y'y'$ intensity anisotropy for the ordering-induced phonons. From this point of view the ground lattice state of the "thick" sample is more "'ordered" (in relation of the CuPt*B* structure) at room temperature than that of the "thin" sample. The existence of differently "ordered" lattice states probably results from the different lattice symmetry of the substrate and alloy film. The resulting symmetry misfit strains will act to move the long-range ordered atoms from their exact trigonal lattice sites. For the "thin" sample such strains dominate, so that the ground state of "thin" sample is "disordered" at room temperature.

The observed changes in Raman intensities can be well described in terms of the changing of the parameter Δ only (see Table 1). Thus the fact, that we observed the changes in the Raman intensity of the long-range ordered $\mathrm{Ga_{0.5}In_{0.5}P}$ only in the $y'y'$ configuration has clear connection with the rearrangements of the trigonal lattice sites.

The Raman intensities of the "disordered" lattice state correspond to a decrease of the parameter Δ for all ordering-induced phonons. This is naturally to connected with the shifting of the atoms situated in the ordered trigonal arrangement to new positions what in turn leads to the changing displacement amplitudes for phosphorus atoms. i.e. parameter Δu_z.

5 Conclusion

In conclusion, we have observed the martensitic transition in epitaxial layers of spontaneously ordered semiconductor alloys $\mathrm{Ga_{0.5}In_{0.5}P}$. The transition is revealed as a strong dependence of the intensity of the order-induced Raman bands on the thermal treatment of the alloy. Our bond polarizability model analysis shows, that the observed Raman spectra behavior can be described in terms of the rearrangement of trigonally-ordered lattice sites, providing an excellent description of the RS of spontaneously ordered $\mathrm{Ga_{0.5}In_{0.5}P}$ alloys and allowing to explain their changes due to thermal treatment.

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