Optical Phonons of Superlattice Phases in Spontaneously Ordered Semicondutcor Alloys

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Raman scattering (RS) and infra-red reflectivity (IR) spectra have been used for investigation of phonons in spontaneously ordered $Ga_xIn_{1-x}P$ ($x \sim 0.5$) and $Ga_xIn_{1-x}As$ ($x \sim 0.2$) epitaxial layers grown by MOVPE method on (100) and (110) GaAs sbstrates. We perform calculations of atomic displacements, spatial and directional phonon dispersion for the {111}-GaP/InP and {001}-GaAs/InAs MSLs in Valence Overlap Shell model (VOSM) using for corresponding constituents parameters of bulk materials. For both alloys phonon bands of corresponding ordered domains have been identified in RS and IR spectra. It is shown that investigation of phonon spectra provide information about local bonding, microstructure and transport properties of partially ordered semiconductor alloys.

I. Introduction

It is well known that nearly all ternary III-V alloys $A_xB_{1-x}C$ can have structures with partial ordering of atomic arrangement what leads to new features in optical and transport properties differing from those of random alloys[1]. Electron diffraction investigations have shown that such spontaneously ordered alloys exhibit several types of ordered structures and can have different degrees of the order depending on growth conditions and type of alloy system. For epitaxial films grown on (001) substrates the most commonly observed ordered structure is $[\bar{1}11]$- and $[1\bar{1}1]$-$(AC)_1(BC)_1$ monolayer superlattice ($CuPt_B$-type structure). For (110) substrates the [001]-$(AC)_1(BC)_1$ monolayer superlattice (CuAu-I type structure) have been observed for some alloys. The other type of ordered structures such as chalcopyrite and famatinite have been observed only in few cases. The main features induced by the ordering of the crystal lattice in the electronic spectra have been intensively studied on example of $Ga_{0.5}In_{0.5}P$ alloys having strong CuP_Bt-type ordering[1,2]. However up to now very little work have been reported relating to variation of phonon spectra of this and other semiconductor alloys due to the ordering.

Here we present the results of investigations of Raman scattering (RS) and infra-red reflectivity (IR) spectra of spontaneously ordered $Ga_xIn_{1-x}P$ ($x \sim 0.5$) and $Ga_xIn_{1-x}As$ ($x \sim 0.2$) alloys grown by MOVPE method on (100) and (110) GaAs substrates and results of lattice dynamical calculations for the {111}-$(GaP)_1(InP)$, and {001}-$(GaP)_1(GaAs)$, monolayer superlattices (MSLs). For both alloys phonon bands of corresponding MSL ordered domains have been identified in RS and IR spectra. We also presented the first Raman observation of optical phonons of $[\bar{1}10]$ - $(GaP)_2(InP)_2$ superlattice (SL) in $Ga_xIn_{1-x}P$ ($x \sim 0.5$) layers grown on (110) GaAs substrate. It is shown that vibrational spectra provide information about local bonding microstructure and transport properties of partially ordered semiconductor alloys.

II. Experimental method

Undoped and Si-doped $Ga_xIn_{1-x}As$ ($x = 0.7 - 0.9$) and $Ga_xIn_{1-x}P$ ($x = 0.51 - 0.53$) epitaxial layers (0.3-1 μm thickness) were grown on (001) and (l l0) GaAs substrates by atmospheric pressure MOVPE at temperatures 650-700°C. The alloy composition was obtained from X-ray diffraction and microanalysis. The density of free electrons was determined from Hall measurements. The degree of the $CuPt_B$-type ordering for $Ga_{0.5}In_{0.5}P$ epilayers have been established from PL

spectra. The existence of $(GaP)_2(InP)_2$ superlattice (SL) was established by X-ray reflections of $(h\pm1/2, k\pm 1/2, 1)$ type and photoluminescence anisotropy[3].

The Raman spectra were measured in the the backscattering geometry using double monochromator U1000 and excited with 514.5 nm Ar^+-ion laser at 300 K as described in [4]. We used polarization geometries $z(xy)\bar{z}$, $z(xx)\bar{z}$, $z(x'x)\bar{z}$ and $z(y'v')\bar{z}$ where z, x, y, x', and y' are the [001], [100], [010], [$\bar{1}$10] and [110] directions respectively. IR spectra were measured on an LAFS-1000 Fourier spectrometer. The method of the determination of free-electron effective mass from phonon-plasmon spectra were described in [5].

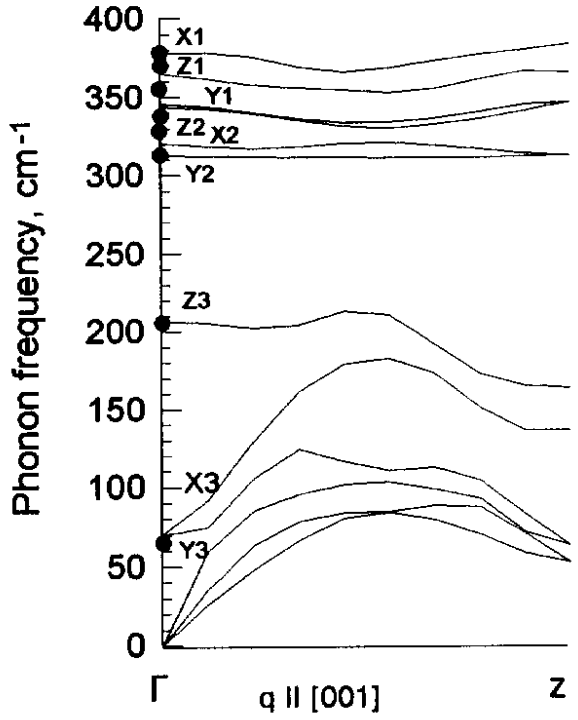

Figure 1. Phonon dispersion curves for $\{-111\}$ $(GaP)_1(InP)_1$ MSL along [001] direction of Zinc blende structure calculated in VOSM. Optical phonon polarization vectors (in MSL coordinales: $Z \parallel \{-111\}$ $X \parallel \{1-12\}$ $Y \parallel \{110\}$) for zone center are indicated. The dots shows frequency values obtained from experimental RS spectra.

We perform calculations of atomic displacements spatial and directional phonon dispersion for the $\{111\}$-$(GaP)_1(InP)_1$ and $\{001\}$-$(GaAs)_1(InAs)_1$ MSLs in Valence Overlap Shell model (VOSM) using for corresponding consistuents bulk parameters [see ref. in 6] and condition of conservation of bulk bond lengths.

$\{111\}_B$-MSL in $Ga_{0.5}In_{0.5}P$ alloys grown on (001) substrates

It has been established that backscattering diagonal polarization of RS of $Ga_{0.5}In_{0.5}P$ alloys has strong anisotropy of $\{110\}$ directions due to CuPtB-type ordering. According to Raman selection rules Z, X modes (see Fig. 1) of $CuPt_B$-type structure are allowed in $(x'x')$ while Y ones in $(y'y')$ polarizations. Polarization anisotropy and bands due to phonons of ordered domains are directly observed in difference $(x'x')/(v'v')$ spectra obtained from substraction of corresponding experimental ones (Fig. 2). As can be seen from Fig. 2 difference $(x'x'/(v'v')$ spectra shows high sensitivity to microstructure of spontaneously ordered $Ga_{0.5}In_{0.5}P$.

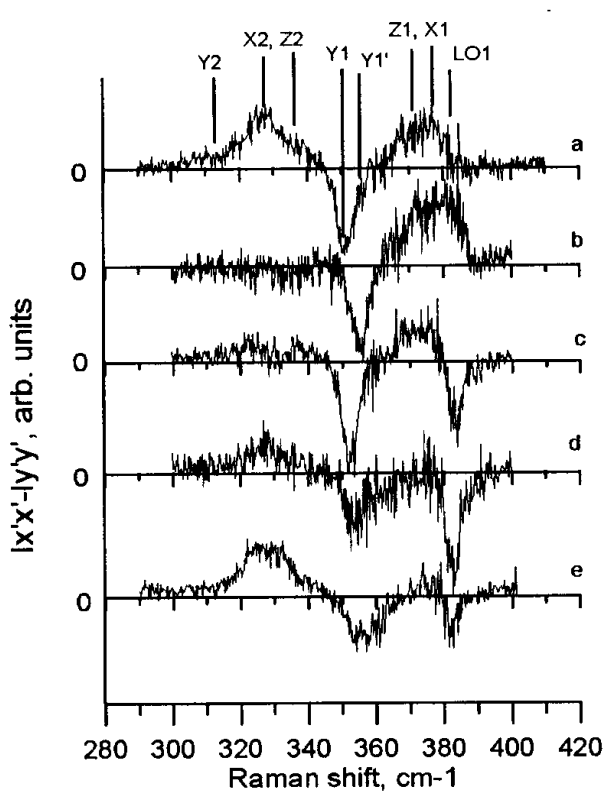

Figure 2. Comparison of difference $x'x'/y'y'$-polarization Raman spectra ($x' \parallel [110]$ $y' \parallel$ [-110]) of $Ga_{0.5}In_{0.5}P$ epilayers with different degrees of the order (decreased from a to e).

Using polarization anisotropy nine bands due to optical phonons of spontaneously organized $\{111\}$ $(GaP)_1(InP)_1$ MSL have been identified in Raman spectra of highly ordered $Ga_{0.5}In_{0.5}P$ epilayers. In the sample with the low degree of the long-range order the band

(40 cm^{-1}) due to an anti-phase boundaries atomic vibrations have been observed. This vibration can be considered as folded acoustic $(GaP)_1(InP)_1$ MSL phonons. The splitting of Yl mode on two component having possible origin from phase separation effects and local strain induced breaking of zinc blende Raman polarization selection rules for LO_1-phonon bauld (GaP-type vibration of disordered clusters) have been obtained (Fig. 2).

Lattice dynamical calculations and fitting to experimentally determined frequency values (Fig. 1) have shown that used VOSM predicts trigonal stretching of MSL unit cell respectively to zinc blende structure.

{110} $(GaP)_2(InP)_2$ SL in $Ga_{0.5}In_{0.5}P$ alloys grown on (110) substrates

The unit cell of {110} $(AC)_2(BC)_2$ SL structure can be obtained by doubling of CuPt-type structure unit cell along [001] direction. So the corresponding phonons can be considered as folded from Brillouin zone boundary of CuPt-type structure.

We identify phonon bands of $[\bar{1}10]$ $(GaP)_2(InP)_2$ SL in comparison of Raman spectra measured in xx, xy', yy' and $y'x$ polarizations (see Fig. 3). According to the Raman polarization selection rules for zinc blende structure the only TO phonons are allowed in backscattering geometry for (110) surface[7].

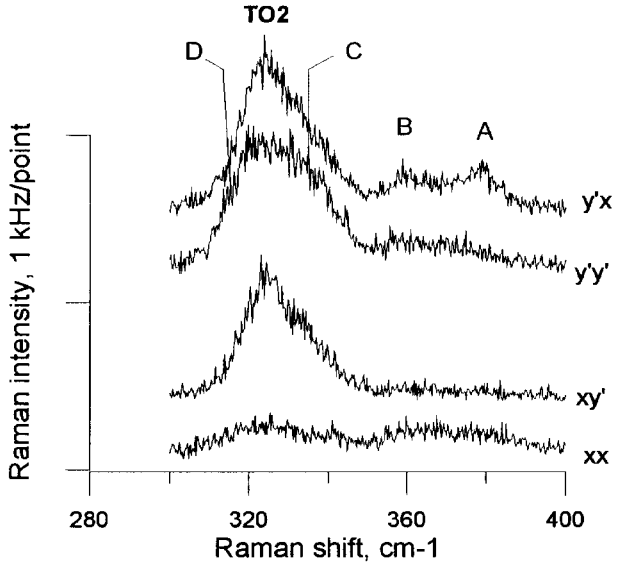

Figure 3. Raman spectra of $Ga_{0.5}In_{0.5}P$ epilayers grown on (110) GaAs substrate.

Three of four presented polarizations are allowed for TO phonons. They are xy', $y'y'$ and $y'x$. In experimental spectra (see Fig. 3) there are only one intense broad band at 325 cm^{-1} (TO_2) which observed in these configurations. Except TO_2 band we can clearly see in Fig. 3 the weaker bands (A B in x'y and C in y'y polarizations). These bands are seen only in single polarization and thus can be assign to phonons of ordered domains.

[001] MSL in $Ga_{0.8}In_{0.2}As$ alloys

For $Ga_{0.8}In_{0.2}As$ alloys grown on (001) and (110) substrates the existence of ordered $GaInAs_2$ complexes have been established from RS and IR spectra. The evidence of such complexes for epilayer

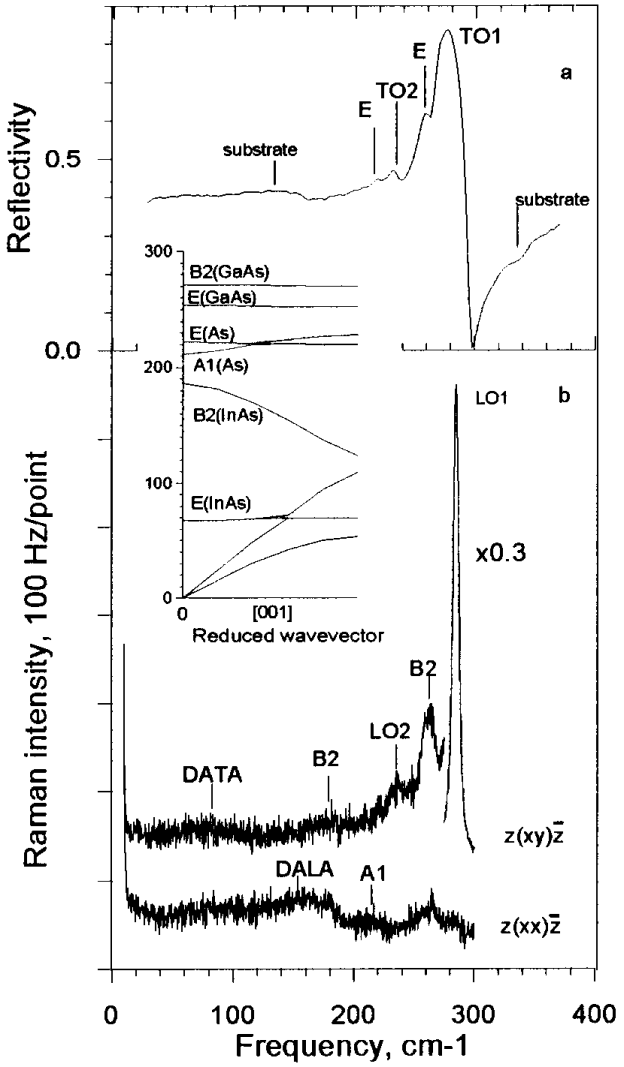

Figure 4. IR and RS spectra of $Ga_{0.8}In_{0.2}As$. In the insert at the center the spatial dispersion the [001]-wave vector phonons of [001] GaAs/InAs MSL calculated in shell model are presented.

grown on (001) oriented substrate are B2 bands at 180 and 260 cm^{-1} in (xy) A_1 at 211 cm^{-1} in (xx) polarizations of RS and E maxima at 217 and 257 cm^{-1} in IR spectra (Fig. 4). From the measurements of the intensities of the phonon bands and the calculations of Raman lineshape function in molecular model[4] it was established that in investigated $Ga_{0.8}In_{0.2}As$ layers major part of In atoms are bounded to the ordered complexes and that there is a considerable charge transfer from In-As to Ga-As bonds. The lattice-dynamical calculations (see Fig. 4) and analysis of symmetry of vibrations IR and Raman selection rules showed that most probable structure of the ordered $GaInAs_2$ complexes is CuAu-I with the strong short-range character.

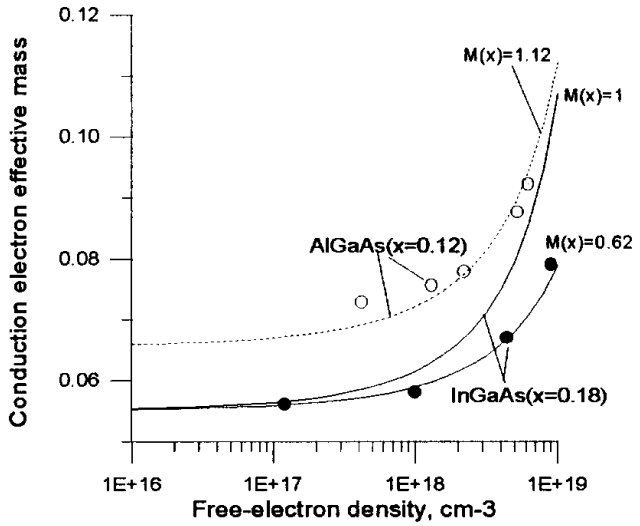

Figure 5. RS measured (dots) and Kien model calculated (curves) conduction electron effective mass versus free-electron (density for $Ga_{0.8}In_{0.2}As$ and $Al_{0.12}Ga_{0.88}As$.

The dependence of an electron effective mass (m^*) on the free-carrier density have been measured from the phonon-plasmon Raman spectra of n-$Ga_{0.8}In_{0.2}As$ $(n = 10^{17} - 10^{19}$ $cm^{-1})$. The measured dependence were fitted according to expression given by Kein model (see Fig. 5): $1/m^* = (1/m_0^*)(1 - \frac{2\Phi}{E_g} * M(x))$ in which we introduced the function $M(x)$ describes mixing of bands by alloy disorder. We obtained $M(x) =$ 0.62 for $Ga_{0.8}In_{0.2}As$ (in contrast to 1.12 one for $Al_{0.12}Ga_{0.88}As$) what indicates on decreasing of non-parbolicity of the conduction band and reflects to our opinion partial ordering crystal lattice effects.

In conclusion we observed the phonon bands of [001], $[\bar{1}10]$ and $\{111\}_B$ SL domains in RS and IR spectra of $Ga_{0.5}In_{0.5}P$ and $Ga_{0.8}In_{0.2}As$ alloys grown by MOVPE on (001) and (110) GaAs substrates, made calculation of lattice dynamics of ordered ternary structures and showed that vibrational spectroscopy provide information about microstructure, local bonding and transport properties of partially ordered semiconductor alloys.

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