Multi-Phonon Raman Scattering

in GaAs/$Al_{0.28}Ga_{0.72}As$ Super-lattice

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Abstract

Raman scattering measurement of GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice has been performed by an incident light with the wave-vector perpendicular to super-lattice growth axis at room temperature. Several peaks in Raman Scattering spectrum are observed. We think that the peak at 290 cm^{-1} may be caused by emission of a longitudinal optical phonon in GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice**,** the peak at 584 cm^{-1} by emission of two ones, and the peak at 876 cm^{-1} by emission of three ones. The multi-phonon Raman scattering may be resulted from the folded optical phonons in super-lattices.

Key-Words: **Multi-phonon Raman scattering; Folded optical phonons; Super-lattice**

1. Introduction

It is of interest to study the interaction between light, i.e. an electromagnetic wave, and lattice waves resulted from vibrations of atoms in super-lattice or between lattice waves and the electron waves propagating in super-lattice**.** For this purpose ones usually employ Raman scattering technique.

The phonon fold effects in super-lattice have been investigated [1,2] . Due to the fact that dispersion relation for optical phonons in bulk material is nearly **q**-independent in long wave region, the ranges of the frequency of optical phonons in two different materials constituting super-lattice cannot be overlapped. Therefore the optical phonons in super-lattice are confined modes of optical vibrations. In the article, we present the fold effects for optical phonons in GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice and in terms of the points of view explain the peaks in Raman scattering spectrum measured in experiments.

2. Sample preparation and experiment results

A GaAs layer doped with Si to 2×10^{18} cm^{-3} with a thickness of 1μm (bottom contact layer) was firstly grown on semi-insulating GaAs substrate by molecular beam epitaxy (MBE) technique. Then a GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice structure with 50 periods was grown. Each period of super-lattice structure consists of a 4.8nm well of GaAs (Si-doped n = 1×10^{18} cm^{-3}) and a 10 nm barrier of $Al_{0.28}Ga_{0.72}As$. Finally, a Si-doped GaAs layer (n = 2×10^{18} cm^{-3}) with 0.5 μm thickness was grown as a top contact layer.

The super-lattice structure grown by MBE was processed into a rectangle sample. Using back--scattering geometry, a beam of incident light with diameter of 1μm illuminates on one side of sample in the direction perpendicular to super-lattice growth axis, as shown in Fig.1(a). Raman

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spectra were collected at confocal Raman microspectroscopy (British Renishaw, RM2000) in the range of 200–1750 cm^{-1}, with NIR 782 nm laser whose power was maintained at 25 mW and the spectral resolution was less than 2 cm^{-1}. Spectrometer scans, data collection and processing were controlled by a personal computer.

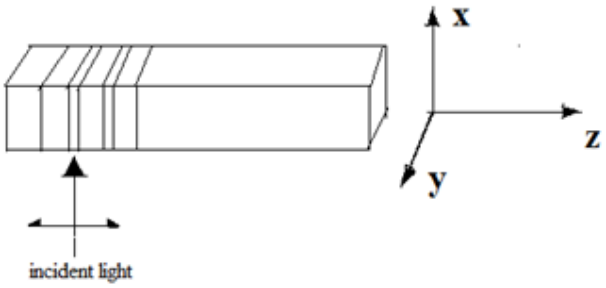

Fig.1(a) The diagram showing the direction of incident light in the measurement of Raman scattering .

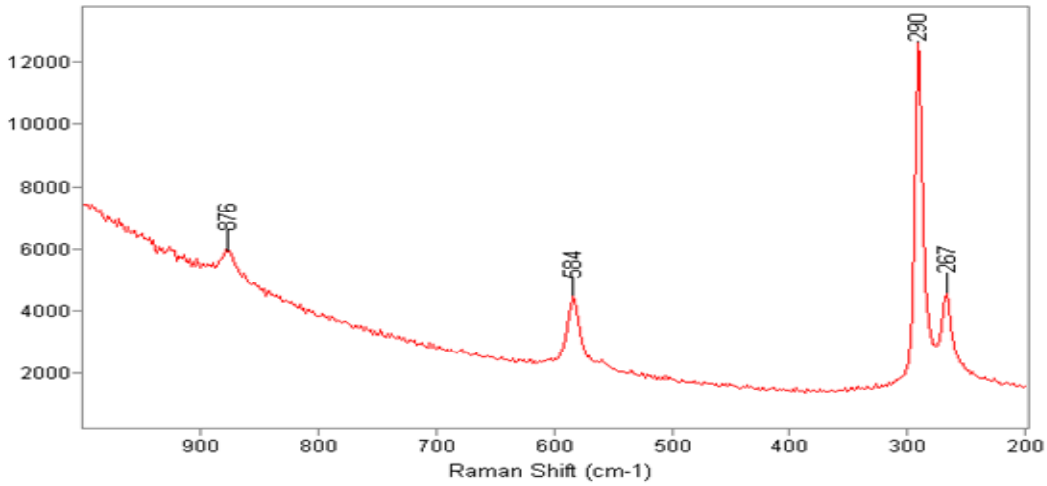

Fig. 1(b). Raman scattering spectrum for $Al_{0.28}Ga_{0.72}As$ super-lattice

3.Resuts and discussion

Fig.1(b) shows measured Raman scattering spectrum for GaAS/$Al_{0.28}Ga_{0.72}As$ super-lattice ,in which vertical axis is Raman intensity (units: Counts).From Fig.1(b) we observe several scattering peaks which are located at 267cm^{-1} , 290 cm^{-1}, 584 cm^{-1} , and 876 cm^{-1}, respectively.

For GaAs/AlGaAs super-lattice（the growth axis **along** z direction）, z- polarized optical phonon wave vectors are given by $q = m\pi/d$, where d is the period of super-lattice, m integer. In the D_{2d} point group of the super-lattice, the z vibrations belong either to the A_1 (m even) or to the B_2 (m odd) representations. The Raman tensors for A_1 and B_2 phonons with respect to the (x,y,z) crystal axes are given by [3]

$$R_{A1} = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} \quad (1), \qquad R_{B2} = \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (2)$$

If we use the backscattering configuration in the $X(Z,\ Z)\bar{X}$, the differential scattering cross-section for A_1 phonons can be written as

$$\frac{d\sigma}{d\Omega} = \mathbf{A}(\boldsymbol{a}_i \cdot \mathbf{R} \cdot \boldsymbol{a}_s)^2 = \mathbf{A}\left[\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \cdot \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}\right]^2 = \mathbf{Ab^2} \neq \mathbf{0} \ , \qquad (3)$$

where a_i and a_s is the unit vector in the direction of polarization for incident light and for scattered one, respectively. We can see from equation (3) that the A_1 phonons are Raman active. Likewise, we can derive that the B_2 phonons are Raman un-active for the backscattering configuration mentioned above. Therefore, the A_1 phonons can be observed if measuring Raman scattering for the configuration in the $X(Z,\ Z)\bar{X}$. But the B_2 phonons cannot be done.

The dispersion relation of longitudinal optical phonons for a linear chain model lattice whose every unit cell contains two different atoms can be represented by [4]

$$\omega^2 = D(\frac{1}{m} + \frac{1}{M}) + D[(\frac{1}{m} + \frac{1}{M})^2 - \frac{4}{Mm}\sin^2\frac{qa}{2}]^{1/2} \quad , \qquad (4)$$

where M and m stands for the mass of a heavy and a light atom , respectively, D is force constant between neighboring atoms, a lattice constant , and q phonon wave-number vector .

For a linear chain GaAs material in which the mass of an atom of **As** is M=75 amu and of **Ga** m = 70 amu**,** we obtain from equation (4) that

$$\omega\ (q=0) = 0.235\ D^{1/2} \quad \text{and} \quad \omega(q = \pi / a) = 0.169\ D^{1/2}. \qquad (4\text{-}1)$$

Similarly, for a linear chain AlAs material in which the mass of an atom of Al is m=27amu, it follows from equation (4) that

$$\omega^*(q=0) = 0.317D^{*1/2} \quad \text{and} \quad \omega^*(q = \pi / a) = 0.272D^{*1/2} \ , \qquad (4\text{-}2)$$

where ω^* and D* is the frequency of optical phonon and force constant between neighboring atoms in AlAs , respectively. Using linear interpolation, the ternary material parameters can be derived from binary material ones [5] . Hence, for a linear chain $Al_xGa_{1-x}As$ we can write as

$$\omega^{**} = x\omega^* + (1\text{-}x)\omega, \quad D^{**} = xD^* + (1\text{-}x)D\ , \qquad (4\text{-}3)$$

where ω^{**} and D** is the frequency of optical phonon and force constant between neighboring atoms in $Al_xGa_{1-x}As$, respectively. Taking x=0.28 and D* ≈ D, it follows from equation (4-3) that

$$\omega^{**}(q=0) = 0.258D^{1/2} \quad \text{and} \quad \omega^{**}(q = \pi / a) = 0.198D^{1/2}. \qquad (4\text{-}4)$$

The optical phonon dispersion relations calculated from equation (4)，(4-1) , and (4-4) are plotted in Fig. 2. in which curve (a) and (b) represents the dispersion relation of linear chain of GaAs and of $Al_{0.22}Ga_{0.78}As$, respectively.

The value of $q = \pi/a$ (a is lattice constant)for GaAs and/or $Al_{0.28}Ga_{0.72}As$ is estimated to be about $10^8 cm^{-1}$. Moreover, we can see from Fig.2. that the dependence of the optical phonon frequency on wave-number vector q is rather weak for bulk GaAs and/or for $Al_{0.28}Ga_{0.72}As$ and that it is negligible if q is less than $10^6\ cm^{-1}$ in which the wave-numbers of infrared or visible light is located. Due to the fact that dispersions of optical phonons of bulk GaAs is overlapping with that of $Al_{0.28}Ga_{0.72}As$ in the frequency region between ω_h and ω_L , here ω_h and ω_L is the maximum and the minimum of frequency of propagation mode , respectively . It gives rise to

the modes propagating in GaAs /$Al_{0.28}Ga_{0.72}As$ super-lattice, but the modes below ω_L are called confined GaAs-like ones which is localized in GaAs layers and modes above ω_h are called confined AlAs-like ones which in $Al_{0.28}Ga_{0.72}As$.

For GaAs / $Al_{0.28}Ga_{0.72}As$ super-lattice with a period d , artificially imposing the periodicity leads to a reduction of the first Brillouin zone in the K_z –direction from $-\pi/a \leq K_z \leq +\pi/a$ to $-\pi/d \leq K_z \leq +\pi/d$. Due to the folding back of optical phonon dispersion relation of the bulk GaAs and/or $Al_{0.28}Ga_{0.72}As$ material onto the first Brillouin zone ranging from $q = 0$ to $q = \pm\pi/d$, it may happen that some "mini-gaps" in the dispersion relation open at the crossing points at the center($q = 0$) and at the boundary of the Brillouin zone $(q = \pm\pi/d)$ if there is a difference of masses of two atoms per unit cell (i.e. $M \neq m$), thus forming the dispersion relation of optical phonons of GaAs / $Al_{0.28}Ga_{0.72}As$ super-lattice. The difference of frequency of the optical phonons between at $q = 0$ and at $q = \pm\pi/d$ for a branch of dispersion relation of GaAs / $Al_{0.28}Ga_{0.72}As$ super-lattice is so small that it can be neglected. Therefore, we can write as follows

$$\omega_{ph,q\approx 0} = \omega_{ph,q=\pm\pi/d} . \qquad (5)$$

It is known that the state density of phonons for two dimension systems can be expressed by[6]

$$G(\omega) = \frac{1}{(2\pi)^2}\int \frac{ds}{\nabla_q \omega(q)} . \qquad (6)$$

For optical phonons propagating in GaAs/$Al_{0.22}Ga_{0.78}As$ super-lattice, their frequency ω is independent of q in the vicinity of $q = 0$, i. e. , $\nabla_q \omega(q)_{q\approx 0} = 0$. This means that there is a maximum of state density of phonons in the vicinity of $q = 0$. Furthermore, the periodicity of super-lattice makes the derivative of frequency of phonons at the boundary of Brillouin zone ($q = \pm\pi/d$) with respect to wave-vector be zero [7], i.e.,

$$\nabla_q \omega(q)_{q=\pm\pi/d} = 0 \quad \text{or} \quad \nabla_q [\omega(q)_{q=+\pi/d} + \omega(q)_{q=-\pi/d}] = 0 . \qquad (7)$$

It follows from formula (7) that there is a maximum of state density of phonons in the vicinity of $q = \pm\pi/d$. The analysis mentioned above shows that there is a maximum of the probability of occurring Raman scattering caused by emission of phonons in the vicinity of at $q = 0$ and/or at $q = \pm\pi/d$.

In terms of optical phonon folding and high scattering probability at $q = \pm\pi/d$ for GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice , we will give in the following an explanation on several peaks in Raman scattering spectrum shown Fig.1(b).

（1）In consideration of the incident light with wavelength λ_v=782nm in vacuum and GaAs with refractivity n = 3.5, its wave-number in GaAs material is $K = 2\pi/\lambda = n\bullet 2\pi/\lambda_v = 3\times 10^5$ cm^{-1} ($\lambda=\lambda_v/n$) which locates the range from $q = 0$ to $q = \pm\pi/d$ ($\pi/d \approx 10^6\ cm^{-1}$).Obviously, the wavelength of the incident light and of optical phonon located the range from $q = 0$ to $q = \pm\pi/d$ is approximately equal or the difference between the two wavelengths is in the range of one order of magnitude. According to the wave theory, the incident light interacts strongly with the optical phonons in first Brillouin zone of GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice, or from the points of view of quantum mechanics, Raman scattering probability in the vicinity of the positions, at $q = 0$ or at $q = \pm\pi/d$, at which there is a maximum value of state density of phonons, is maximum.

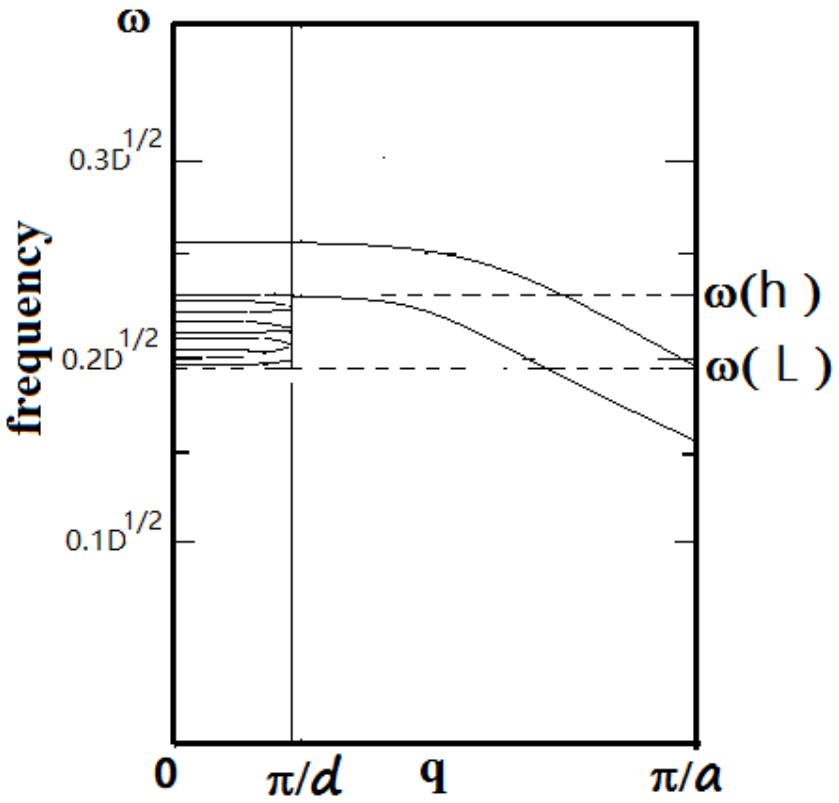

Fig.2. The dispersion relations of optical phonons of linear chain of GaAs (a) and of $Al_{0.28}Ga_{0.72}As$ (b) , and optical phonon folding for GaAs/ $Al_{0.28}Ga_{0.72}As$

If the wave number vector of an incident light is perpendicular to GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice growth axis, it can interact with long longitudinal optical waves ($q \approx 0$) in the super-lattice due to their polarization direction being the same, thus leading to Raman scattering by emission of an optical phonon and creation of a photon, and the peak with frequency shift of 290cm^{-1} in Fig.1(b) may be resulted from the scattering. It was Known that the frequency of longitudinal optical modes for the GaAs is equals to 292cm^{-1} [8], i.e., The energy of a longitudinal optical phonon is 36meV. The difference of 2cm^{-1} is resulted from influence of interface modes for GaAs/$Al_{0.28}Ga_{0.72}As$. Based on energy and momentum conservation in Raman scattering, it can be expressed as

$$\hbar\omega_s = \hbar\omega_i - \hbar\omega_{ph} \quad (8)$$

$$\hbar K_s = \hbar K_i - \hbar q \quad (9)$$

where symbol "ω_s" and "ω_i " is the frequency of scattered and of incident light， respectively, ω_{ph} is frequency of phonons, and q wave-number vector of phonons. From equation (8) the energy of an optical phonon emitted in Raman scattering can be calculated by

$$\hbar\omega_{ph} = \hbar(\omega_i - \omega_s) = \hbar\Delta\omega = hc\left(\frac{1}{\lambda_i} - \frac{1}{\lambda_s}\right) = hc(\nu_i - \nu_s) = hc\Delta\nu \quad (10)$$

Substituting the value of 290cm^{-1} for $\Delta\nu$ ($\nu = 1/\lambda$) in formula (10), it follows that $\hbar\omega_{ph} =$ 36meV. It is just the energy of a longitudinal optical phonon in GaAs . Therefore the peak at 290cm^{-1} in Raman scattering spectrum may be resulted from emission of a longitudinal optical

phonon.

Comparing $k_i(k_i = 2\pi/\lambda_i = n \cdot 2\pi/\lambda_v = 3 \times 10^5\,cm^{-1})$ with q $(q = 2\pi\Delta\nu)$, it can be seen that k_i is far more than q. According to the rule of the addition of vectors, it can be derived from equation (9) that the direction of the wave-vector K_s of the scattered light is nearly anti-parallel to that of the wave-vector k_i of the incident one.

In addition, Z vibrations of atoms in GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice could also form transverse optical waves propagating in x or y direction. The incident photons interacting with transverse optical wave of long wavelength (q≈0) would induce Raman scattering, thus resulting in the peak with frequency shift of 267cm^{-1}, as shown in Fig.1(b). Comparing it with transverse optical waves with wave number $269cm^{-1}$ [8] for GaAs , obviously, there is a difference of 2cm^{-1} , it is resulting from the influence of interface modes of GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice(9) .

（2）The peak with frequency shift of 584cm^{-1} , shown in Fig.1(b),which is double of the optical phonon frequency of 292cm^{-1} for GaAs, may be resulted from the successive emission of two phonons in Raman scattering due to photons interacting with the phonons in the vicinity of the boundary of the first Brillouin zone of GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice. According to energy and momentum conservation in Raman scattering, it can be expressed as

$$\hbar\omega_s = \hbar\omega_i - 2\hbar\omega_{ph} \qquad (11)$$

$$\hbar\boldsymbol{k_s} = \hbar\boldsymbol{k_i} - \hbar q_{1.\approx+\pi/d} - \hbar q_{2.\approx-\pi/d} \qquad (12)$$

From equation (11) the energy of two phonons emitted successively in Raman scattering is given by

$$2\,\hbar\omega_{ph} = \hbar(\omega_i - \omega_s) = \hbar\Delta\omega = hc\Delta\left(\frac{1}{\lambda}\right) = hc\Delta\nu \qquad (13)$$

Substituting the value of 584cm^{-1} shown in Fig.1(b) for $\Delta\nu$ in formula (13), we obtain $2\hbar\omega_{ph}$ =72meV. This value is double of the energy of an optical phonon in GaAs. Therefore, we believe that the peak at 584cm-1 in Fig.1(b) may be resulted from successive emission of two optical phonons in Raman scattering.

(3) For the GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice whose parameters are given as above, its band gap energy can be calculated to be $E_g(sup.)$=1.522eV(10) . It is known that the energy of an incident photon（light wavelength of 782nm) used in Raman experiment is equal to 1.586eV. If, in the first Raman scattering process, the energy of an optical phonon emitted is equal to 36meV, the energy of a photon created simultaneously should be 1.550eV. Supposing that the direction of polarization of the photons created in the first Raman scattering is perpendicular to the interface of GaAs /$Al_{0.28}Ga_{0.72}As$, the created photons can make electrons on level E_{hh}(heavy hole energy) in valence band excite into quantum wells in conduction band of super-lattice. We estimate that these excited electrons should lie on the level about 28meV above ground state level E_0 in quantum well as shown Fig.3. The wave-numbers of the electrons lying on the excited states in the quantum wells can be calculated by $Q = (2m^*\Delta E/\hbar^2)^{1/2}$, where ΔE is kinetic energy of an electron, m^* electron effective mass in GaAs, and $\hbar$ Planck constant divided by 2π. Taking ΔE = 28meV and $m^* = 0.067m_0$, the calculated wave-numbers of the electrons are Q =2 ×10^{6}cm^{-1} which is just equal to the value of π/d , i.e. , the wave-numbers of phonons at $q = \pi/d$ (d=14.8nm, the period of super- lattice).

This means that the excited electrons would interact strongly with phonons in the vicinity of $q = \pm\pi/d$, emitting successively two optical phonons and recombining with a hole in valence band, simultaneously creating a photon, consequently, resulting in the peak with frequency shift of

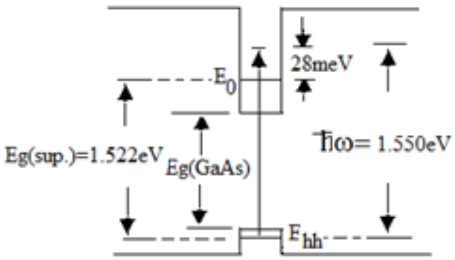

Fig.3. Schematic representation of multi-phonon Raman scattering for GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice

876cm^{-1} shown in Fig.1(b). It is triple of the optical phonon frequency of 292cm^{-1} for GaAs. Based On energy and momentum conservation in Raman scattering process, it can be written as

$$\hbar\omega_s = \hbar\omega_i - \hbar\omega_{ph,q\approx 0} - 2\hbar\omega_{ph,q\approx\pm\pi/d} \quad (14)$$

$$\hbar K_s = \hbar K_i - \hbar q_{\approx 0} - 2\hbar q_{\approx\pm\pi/d} \quad . \quad (15)$$

For each branch of dispersion relations of longitudinal optical phonons of GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice, we can write as

$$\omega_{ph} = \omega_{ph,q\approx 0} = \omega_{ph,q\approx\pm\pi/d} \quad . \quad (16)$$

Thus it follows from equation (14) that

$$3\,\hbar\omega_{ph} = \hbar(\omega_i - \omega_s) = \hbar\Delta\omega = hc\Delta\left(\frac{1}{\lambda}\right) = hc\Delta\nu \quad . \quad (17)$$

Substituting the value of 876cm-1 for $\Delta\nu$ in formula (17), total energy of optical phonons emitted in the Raman scattering is given to be $3\hbar\omega_{ph} = 109meV$ which is equal to triple of the energy of a longitudinal optical phonon in GaAs.

4. Conclusions

Since GaAs and $Al_{0.28}Ga_{0.72}As$ are polar materials, their lattice vibrations can produce lattice waves with affixation electric field in the direction of lattice vibrations. Incident light (laser), as an electromagnetic wave, may interact with the lattice waves in GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice.

It is known that polarization direction of longitudinal optical waves propagating along the direction of super-lattice growth axis is perpendicular to interfaces of GaAs/$Al_{0.28}Ga_{0.72}As$. If the direction of wave number vector of incident light is perpendicular to super-lattice growth axis, the incident light may interact with longitudinal optical waves of GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice, thus resulting in Raman scattering by emission of phonons and creation of a photon.

Since folding back of optical phonon dispersion relation, imposed by the period d of the super-lattice, may produce a few of new Raman active modes at the center and at boundary of the first Brillouin zone of GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice, this leads to high Raman scattering probability. Consequently, the multi-phonon Raman scattering are observed in our experiment for GaAs/$Al_{0.28}Ga_{0.72}As$ super-lattice.

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