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Abstract. Making use of the refractive indices for Ge$_x$Si$_{1-x}$ alloys from recent ellipsometric experiments, the acoustic velocities of Ge$_x$Si$_{1-x}$ alloys in Ge$_x$Si$_{1-x}$/Si superlattices have been obtained by Raman shifts of folded longitudinal acoustic phonons. The results near $x = 0.5$ are different from those determined by previous Raman scattering experiments. The origin of the difference is discussed.

The acoustic velocities of the components in superlattices (SLs) are the basic parameters in studies of SLs, such as characterizations of the SL periods from the Raman shifts of the folded acoustic phonons [1,2] and measurements of the photoelastic constants from the intensities of the folded acoustic phonons [2,3]. By means of light scattering, the acoustic velocities in bulk materials can only be determined from the Brillouin scattering, whereas in SLs it becomes possible to determine acoustic velocities of the components by Raman scattering. One can obtain the acoustic velocities from both the Raman shifts of the folded acoustic phonons and the doublet splits of the m_+- and m_--order folded acoustic phonons.

In the continuum limit the folded acoustic phonon dispersion relation in SLs based on the Rytov model is given by [1,2]

$$\cos(qd) = \cos[\omega(d_1/V_1 + d_2/V_2)] - (\varepsilon^2/2)\sin(\omega d_1/V_1)\sin(\omega d_2/V_2) \quad (1)$$

where

$$\varepsilon = (V_1\rho_1 - V_2\rho_2)/(V_1\rho_1 V_2\rho_2)^{1/2}$$

and where ω is the vibration frequency of the phonon, q the SL wavevector, d_i, V_i and ρ_i are the individual layer thicknesses, acoustic velocities and densities of Ge$_x$Si$_{1-x}$ ($i = 1$) and Si ($i = 2$) layers in SL, respectively, and d is the SL period ($d = d_1 + d_2$).

By using an approximate relation for the SLs studied, $\rho_1 V_1 = \rho_2 V_2$, equation (1) can be rewritten as

$$\omega_{m\pm} = \overline{V}[(2\pi m/d) \pm q] \tag{2a}$$

$$\delta\omega_m = \omega_{m+} - \omega_{m-} = 2\overline{V}q \tag{2b}$$

$$\overline{V} = \frac{V_1 V_2}{(d_2/d)V_1 + (d_1/d)V_2} \tag{3}$$

where $\overline{V}$ is the average acoustic velocity of the SLs, m is the folded order and $\omega_{m\pm}$ is the frequency of m_+- or m_--order folded acoustic phonons. $\delta\omega_m$ is the doublet split of the m_+- and m_--order folded acoustic phonons. The density ρ_1 in the Ge_xSi_{1-x} layers can be estimated by linear interpolation from the following equation:

$$\rho_1 = \rho_{Si}(1 - x) + \rho_{Ge}x . \tag{4}$$

Therefore, V_1 could be obtained by fitting the frequencies of folded acoustic phonons calculated using (1) or (2) with the corresponding experimental values. In addition, V_1 could be obtained from the measured $\delta\omega_m$ with the help of (2b). Comparison of the dispersion relation from (1) with that from (2) has been made in [4], and the results show that for the folded acoustic phonons with q far away from the Brillouin-zone centre and edge the differences between the dispersion relations from (1) and (2) are negligible as compared with the experimental resolution. As a result, the approximation in (2) should not result in significant errors in the V_1 obtained from the doublet splits of the m_+- and m_--order FLAs. Besides, V_1 can also be obtained by linear interpolation between the Si and Ge acoustic velocity values, i.e.

$$V_1 = V_{Si}(1 - x) + V_{Ge}x . \tag{5}$$

The density ρ and acoustic velocity V for Si and Ge used in (4) and (5) are taken to be $\rho_{Si} = 2.33$ g cm^{-3}, $V_{Si} = 8.433 \times 10^5$ cm s^{-1}, $\rho_{Ge} = 5.323$ g cm^{-3} and $V_{Ge} = 4.97 \times 10^5$ cm s^{-1}, respectively.

The acoustic velocities for longitudinal acoustic phonons along [001] of Ge_xSi_{1-x} in Ge_xSi_{1-x}/Si SLs, V_1, at different Ge contents x, have been determined by Raman scattering. The result that values V_1 for $x \leqslant 0.45$ could be estimated by using (5) has been obtained by Lockwood *et al* [5] from Raman shifts of the folded longitudinal acoustic phonons (FLAs), whereas the V_1 for $x = 0.5$ obtained by Brugger *et al* [6] from the doublet split of the m_+- and m_--order FLAs is $(7.5 \pm 0.4) \times 10^5$ cm s^{-1}, which is slightly higher than 6.7×10^5 cm s^{-1} obtained by using the interpolation formula (5). However, we cannot conclude that their results are in conflict with each other, because the linear interpolation is more suitable for Ge-rich or Si-rich alloys and may break down near the middle point, $x = 0.5$. These results for V_1 have been used for the characterization of Ge_xSi_{1-x}/Si SLs [7] and, particularly, the V_1 for $Ge_{0.5}Si_{0.5}$ has been used in the study of the photoelastic properties [8] and effect of acoustic attenuation on light scattering by acoustic phonons in Ge_xSi_{1-x}/Si SLs [9]. But in our study of Ge_xSi_{1-x}/Si SLs with x near 0.5, there always exist systematic errors between the SL periods determined by x-ray experiments and ones obtained from the Raman shifts of FLAs—as we used $V_1 = (7.5 \pm 0.4) \times 10^5$ cm s^{-1} determined in [6], a careful examination of the V_1 for x near 0.5 becomes necessary. In this communication, we will report on the determination of V_1 for x near 0.5 by Raman scattering.

Table 1. A list of the $Ge_x Si_{1-x}/Si$ SLs used in our experiments, d is the SL period, d_1 is the thickness of $Ge_x Si_{1-x}$ alloy layers and N is the period number.

Sample	x	d (Å)	d_1/d	N
S1	0.51	263	0.17	20
S2	0.43	93	0.30	20
S3	0.37	239	0.17	20

The samples studied here are three $Ge_x Si_{1-x}/Si$ SLs, S1, S2 and S3, grown by MBE on Si(001) substrates. The parameters of these samples are listed in table 1. The structure parameters of these SLs were determined by double-crystal x-ray diffraction experiments.

The Raman experiments were performed at room temperature and excited with the Ar^+ laser line of 5145 Å, with the polarization configuration $z(x', x')\bar{z}$ ($z = [001]$, $x' = [110]$); hence only vibrations with longitudinal character are Raman allowed. The samples were kept in a vacuum chamber in order to eliminate air features from the spectra. The scattered light was analysed by a SPEX-1403 double monochromator coupled with the third monochromator, and detected with conventional photon-counting electronics. In backscattering geometry, the scattering wavevector is given by

$$q = 4\pi n/\lambda \tag{6}$$

where

$$n^2 = (d_1 n_1^2 + d_2 n_2^2)/d$$

and where n_1 and n_2 are the refractive indices of the $Ge_x Si_{1-x}$ alloy and Si at the wavelength λ.

In figure 1, curves a, b and c show the Raman spectra of samples S1, S2 and S3, respectively. All spectra show several distinct lines. These lines are very sharp and their widths are limited mainly by the resolution of the experiments, which indicates that these samples have abrupt interfaces and good crystalline quality [10]. The spectral resolution is 0.9 cm^{-1} for spectra a and c and 1.4 cm^{-1} for spectrum b. The experimental Raman shifts, ω_{exp}, of the observed FLAs are listed in table 2. According to the Rytov dispersion relation given as equation (1), the 3_+- and 4_--order FLAs of S1 would peak in spectrum a near 35 cm^{-1}, whereas by the calculation using the model of [3] the intensity of the 4_--order FLA is about 60 times smaller than that of the 3_+-order FLA and too weak to be resolved; hence only a singlet of 3_+-order FLA is observed near 35 cm^{-1}. For the same reason the structure near 45 cm^{-1} in spectrum a is assigned to the singlet of 4_+-order FLA. As mentioned above, the V_1 could be obtained by fitting the frequencies of FLAs calculated using equation (1) with the corresponding experimental values, but due to the experimental error in the measurements there exists an uncertainty δV_1 in the V_1 determined. With the help of (2) and (3), the relative error of V_1 is given by

$$\delta V_1/V_1 = (dV_1 \omega_R)/(d_1 \overline{V} \omega_{m\pm}) \tag{7}$$

where ω_R is the limited spectral resolution and $\omega_{m\pm}$ are the frequencies of FLAs defined by (2). It is obvious from (7) that δV_1 could be reduced by choosing the FLA with

the higher frequency. Utilizing the largest Raman shifts among the experimentally observed FLAs and equation (1), the values V_1 for S1, S2 and S3 have been obtained and the results are listed in table 3. The frequencies ω_{cal} of the FLAs calculated using equation (1) with the velocities given in table 3 are listed in table 2. In addition, the frequencies of FLAs for S1 which are calculated using equation (1) with $V_1 = 7.5 \times 10^5$ cm s^{-1} from [6], ω^*_{cal}, are also listed in table 2. The densities ρ_1 used in the calculation for both ω_{cal} and ω^*_{cal} are from equation (4), but the refractive indices of Ge$_x$Si$_{1-x}$ alloys are all from [11]. Since the refractive indices in [11] were measured with an increment of 0.1 eV energy and only at nine different values of x, the refractive indices used by us are the linear interpolation values. The real part of refractive index for the Ge$_x$Si$_{1-x}$ alloy at wavelengths 5145 Å, 4880 Å and 4579 Å versus Ge content, x, obtained in this way are displayed in figure 2. Comparing the ω_{exp} with both the ω_{cal} and ω^*_{cal} for S1 in table 2 one finds that all the ω_{cal} agree with the corresponding ω_{exp} within the spectral resolution. The discrepancies between the ω^*_{cal} and ω_{exp} are also smaller than the spectral resolution for low-frequency FLAs. However they become larger than the spectral resolution for FLAs with Raman shifts greater than 25 cm^{-1} and become twice as large as the spectral resolution for the 4_+-order FLA. Such large discrepancies probably come from an overestimation of the value V_1. For S2 and S3, all the ω_{cal} agree with the corresponding ω_{exp} within the spectral resolution. The above results indicate that the acoustic velocities of the Ge$_x$Si$_{1-x}$ alloy in S1, S2 and S3 obtained by us from the largest Raman shifts among the observed FLAs are reliable.

Table 2. Experimental and calculated frequencies of FLAs. In the calculation of ω_{cal}, the V_1 are taken to be 6.2×10^5 cm^{-1}, 6.8×10^5 cm^{-1} and 7.4×10^5 cm^{-1} for S1, S2 and S3, respectively. $V_1 = 7.5 \times 10^5$ cm s^{-1} is used for ω^*_{cal}. The limited resolution of the experiments is 0.9 cm^{-1} for S1 and S3 and 1.4 cm^{-1} for S2.

	S1			S2		S3	
m	ω_{exp} (cm^{-1})	ω_{cal} (cm^{-1})	ω^*_{cal} (cm^{-1})	ω_{exp} (cm^{-1})	ω_{cal} (cm^{-1})	ω_{exp} (cm^{-1})	ω_{cal} (cm^{-1})
0	4.5	4.4	4.7				
1−	5.8	5.6	5.8	24.5	23.6	7.0	6.7
1+	14.8	14.4	14.9	33.5	32.8	15.8	15.9
2−	16.0	15.7	16.5	52.5	51.8	18.2	18.2
2+	24.7	24.5	25.6	61.0	61.0	27.0	27.4
3−	25.9	25.7	26.7			29.2	29.4
3+	34.6	34.5	36.0			38.2	38.6
4−		35.8	37.3			10.8	40.8
4+	44.6	44.6	46.4				

The values of V_1 for S1, S2 and S3 SLs estimated by linear interpolation between Si and Ge acoustic velocity values are also listed in table 3. These values agree, within the experimental errors, with those obtained from the largest Raman shifts among the observed FLAs. Therefore, it is concluded that the acoustic velocity of Ge$_x$Si$_{1-x}$ in the range of small x to x near 0.5 can be estimated by linear interpolation with equation (5). The same results have been obtained for $x \leqslant 0.45$ in [5], in which the FLA frequencies calculated using equation (1) with the value V_1 estimated by equation (5) fitted the experiments within the experimental errors. Such a result is also confirmed

Table 3. The acoustic velocity of Ge_xSi_{1-x} alloy obtained from experiments (V_1) and estimated by linear interpolation using equation (5) (V_1^*).

	S1	S2	S3
x	0.51	0.43	0.37
V_1 (10^5 cm s^{-1})	6.2 ± 0.6	6.8 ± 0.5	7.4 ± 0.8
V_1^* (10^5 cm s^{-1})	6.67	6.94	7.15
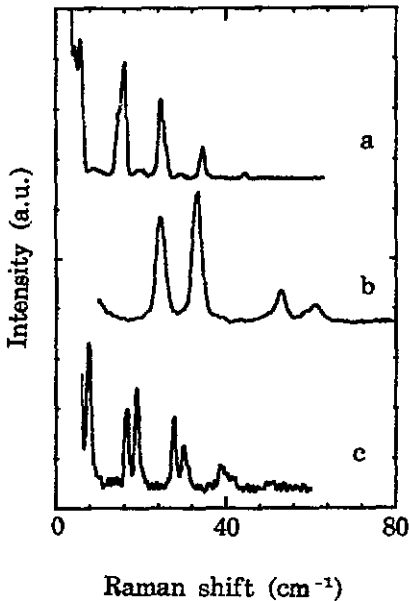
Figure 1. Raman spectrum of samples S1 (a), S2 (b) and S3 (c).
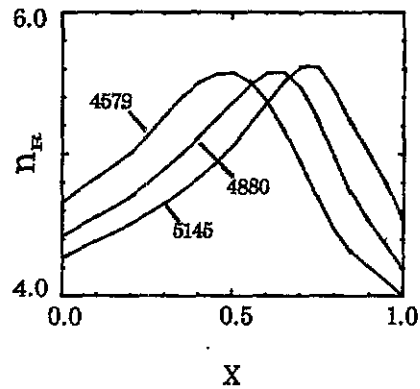
Figure 2. The real part of the refractive indices, n_R, in Ge_xSi_{1-x} alloy versus x at wavelengths 5145 Å, 4880 Å and 4579 Å from [11].

by diffuse x-ray experiments [12]. From these experiments the elastic constants of Ge_xSi_{1-x}/Si alloys with $x = 0.36$, 0.46 and 0.72 have been determined, and thus the values of V_1 can be obtained giving $(7.1\pm0.4)\times10^5$ cm s^{-1}, $(6.8\pm0.4)\times10^5$ cm s^{-1} and $(6.0\pm0.4)\times10^5$ cm s^{-1}, respectively. These acoustic velocities are in good agreement with the values 7.19×10^5 cm s^{-1}, 6.84×10^5 cm s^{-1} and 5.94×10^5 cm s^{-1} estimated from equation (5).

We think that the overestimation of the acoustic velocity of the $Ge_{0.5}Si_{0.5}$ alloy determined in [6] arises from the inappropriate value of n_1 used in the calculation. Due to a lack of experimental data on the refractive index of the Ge_xSi_{1-x} alloy it has been assumed in [6] that the refractive index of the Ge_xSi_{1-x} alloy was approximately equal to that of Si at wavelengths of Ar$^+$ laser lines; this assumption is based on the fact that the refractive index of Ge is close to that of Si at such wavelengths. It is known that the energy of the direct gap for Si is greater than those of all Ar$^+$ laser lines whereas for Ge it is below those of all Ar$^+$ laser lines, and as the Ge content, x, increases, the energy of the direct gap in Ge_xSi_{1-x} alloy will decrease and fall into the energy region of Ar$^+$ laser lines when x is near 0.5 [13]. According to the refractive index curves

for Ge_xSi_{1-x} versus x in figure 2, a large error will be introduced if one assumes that the refractive index of the Ge_xSi_{1-x} alloy is the same as that of Si on the basis that Si and Ge have nearly the same refractive indices. Making use of the $\delta\omega_m$ measured in [6], we calculated V_1 with the refractive index of the Ge_xSi_{1-x} alloy from figure 2 and obtained $V_1 = 6.4 \times 10^5$ cm s^{-1} for $Ge_{0.5}Si_{0.5}$, which is 16% smaller than that determined in [6] with the same experimental $\delta\omega_m$. Considering that the experimental error in V_1 resulting from the measurement resolution of 0.3 cm^{-1} [6] is about 11%, this value of V_1 is in good agreement with the value of V_1 for S1, 6.2×5 cm s^{-1}, obtained in our experiments, as well as the value $V_1 = 6.67 \times 10^5$ cm s^{-1} estimated from equation (5). The same assumption for Ge_xSi_{1-x} alloy refractive indices as mentioned above has also been made in [5], but the effects of the inappropriate value of n_1 have been smeared out by the relatively large experimental resolution, 1.6 cm^{-1} [5]; therefore seemingly reasonable results were obtained in this situation.

In summary, we have determined V_1, the acoustic velocities of Ge_xSi_{1-x} alloys in superlattices, with the help of the experimental refractive indices of Ge_xSi_{1-x} alloys presented in [11], and have come to the conclusion that the method for estimating the acoustic velocity of Ge_xSi_{1-x} in SLs by linear interpolation between Si and Ge acoustic velocity values could be used for x near 0.5. An analysis reveals that the overestimation in the acoustic velocity of the $Ge_{0.5}Si_{0.5}$ alloy, obtained by previous Raman scattering, arises from inappropriate refractive indices used in the calculation.

Acknowledgments

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