# RAMAN STUDY OF STRAIN AND CONFINEMENT EFFECTS IN Si/Ge STRAINED LAYER SUPERLATTICES UNDER HYDROSTATIC PRESSURE

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## ABSTRACT

The effects of strain and confinement on optical phonons in a $Si_{12}Ge_4$ strained layer superlattice grown by MBE on c-Si (001) were studied as a function of hydrostatic pressure (T = 295 K) using Raman scattering. The change of phonon frequency with pressure, dω/dP, for the principal quasi-confined LO mode in the Ge layers is found to be significantly smaller than that for bulk crystalline Ge because the magnitude of biaxial strain decreases in the Ge layers with added pressure and because the Grüneisen parameter of the confined mode is smaller than that of the Γ-point optical phonon. More generally, it is noted that the magnitude of biaxial strain in many strained layer superlattices initially decreases with the application of hydrostatic pressure, making the structures more stable.

## INTRODUCTION

Ultrathin Si/Ge strained layer superlattices (SLS) have been grown recently with high quality crystallinity, by using molecular beam epitaxy (MBE), despite the significant lattice mismatch (~4%) between Si and Ge.[1-2] The electronic properties of Si/Ge superlattices are of particular interest because of the possibility of obtaining quasi-direct gap behavior through a combination of zone folding and strain effects.[3,4] Raman studies of the structural properties of Si/Ge superlattices have yielded useful information on strain, confinement and interfacial disorder.[5-7]

The application of high pressure provides a new method to study the effects of strain and confinement in layered structures. When hydrostatic pressure is applied to a SLS, the lattice mismatch between alternating layers changes because of the different compressibilities of the two materials in these layers, and consequently biaxial strain can be tuned. Moreover, the shift of each confined mode frequency with applied pressure differs from that of the zone-center longitudinal optical (LO) phonon because the Grüneisen parameter varies across the LO phonon dispersion curve. In this work, we study strains in a Si/Ge superlattice by subjecting the SLS to high pressure in a diamond anvil cell (DAC), and then analyzing it by Raman spectroscopy. More details are provided in Ref.[8].

## EXPERIMENTAL PROCEDURE AND RESULTS

The superlattice was grown by MBE on top of a 2700 Å Si buffer layer which had been grown on a Si substrate cut 2° from the [001] plane. The growth temperature was 375 - 400°C. The superlattice consists of 12 monolayers of Si followed by 4 monolayers of Ge ($Si_{12}Ge_4$), repeated 25 times, and is covered by a 140 Å Si cap layer. The SLS substrate was mechanically thinned to 50 μm, and then loaded into a gasketed Mao-Bell diamond anvil cell in order to apply hydrostatic pressure. The pressure (P) in the DAC was determined by the standard ruby calibration scale. Raman spectra of Si/Ge SLS were taken at room temperature using the 4880 Å line from a CW argon ion laser in the backscattering configuration.

The Raman spectrum of this Si/Ge SLS is characterized by the presence of three main peaks, assigned in order of increasing energy to Ge, Ge-Si-like and Si vibrations. Two representative Raman spectra are shown in Figure 1, corresponding to ambient pressure (1 bar) and 62.5 kbar, the maximum applied pressure in the experiment. Only one Ge peak was found, at 308.0 $cm^{-1}$ for P = 1 bar; it was asymmetric with a tail towards lower energy. This peak corresponds to the principal quasi-confined mode in the Ge layers, and is shifted in energy with respect to that in bulk c-Ge (301.3 $cm^{-1}$ at P = 1 bar). The big Si peak near 520 $cm^{-1}$ is from the unstrained c-Si contributed by the cap layer, superlattice Si layers, the buffer layer and the substrate.

The least square straight lines of the Raman shifts of each feature vs. pressure yield $d\omega/dP$ values for each peak. $d\omega/dP$ is 0.31 ± 0.03, 0.45 ± 0.03 and 0.47 ± 0.02 $cm^{-1}$/kbar for the Ge, Ge-Si-like and Si peaks, respectively. For comparison, the Raman shifts vs. pressure for bulk c-Ge and c-Si were also measured in this same pressure range, giving 0.37 ± 0.02 and 0.49 ± 0.02 $cm^{-1}$/kbar for c-Ge and c-Si, respectively. $d\omega/dP$ for the Ge phonon in the SLS is 0.06 $cm^{-1}$/kbar smaller than that in c-Ge.

## ANALYSIS AND DISCUSSION

Lattice dynamics and linear chain model calculations of Si/Ge SLS's [7,9] show that there are confined modes in thin Si layers, and quasi-confined modes in thin Ge layers, even though the Ge optic and Si acoustic modes overlap in energy. There is no biaxial strain in the Si layers because the SLS is commensurately grown on c-Si and the Si layers in the SLS are so thick that confinement effects are small. Consequently, the Si layer Raman peak overlaps that of the cap and buffer layers and it is of no interest here. The observed principal quasi-confined Ge mode is affected by strain and confinement. At ambient pressure, the frequency of the principal confined Ge optic phonon in the SLS ($\omega$) is 6.7 $cm^{-1}$ higher than that of zone center LO phonons in c-Ge ($\omega_0$). The compressive stress in the Ge layer is expected to increase $\omega$ by 15.8 $cm^{-1}$ ($\Delta\omega_{strain}$), suggesting that the quasi-confinement decreases $\omega$ by ~ 9 $cm^{-1}$ ($\Delta\omega_{confinement}$). This conclusion agrees with other experimental results and with an estimate from the LO phonon dispersion curve.[5,7] The measured Raman shift at ambient pressure can be expressed as

$$\omega = \omega_0 + \Delta\omega_{strain} + \Delta\omega_{confinement} \tag{1}$$

Similarly, the change in Raman shift with applied pressure $\delta\omega(P)$ can be attributed to changes due to strain and confinement

$$\delta\omega(P) = \delta\omega_{strain}(P) + \delta\omega_{confinement}(P) \tag{2}$$

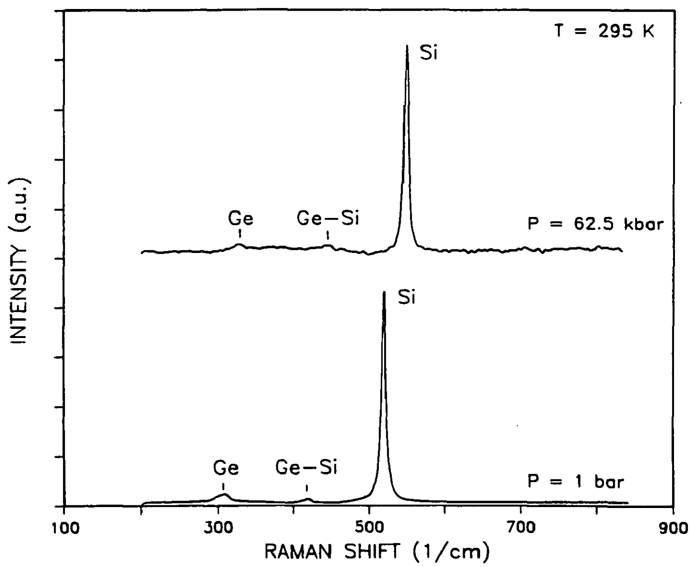


Figure 1. Raman spectra taken at P = 1 bar and P = 62.5 kbar are shown (T = 295 K). The peaks in order of increasing energy are the principal quasi-confined Ge mode, Ge-Si-like mode and Si mode.

The Effect of Strain

The Raman frequency for an optical phonon in Ge layers of the SLS along the [001] direction, in the absence of confinement and interfacial disorder, is

$$\omega = \omega_0 + \frac{1}{2\omega_0}\left[ p\,\varepsilon_{zz} + q\,(\varepsilon_{xx} + \varepsilon_{yy}) \right] \tag{3}$$

where p and q are the Ge deformation potentials defined in Ref. [10], and $\varepsilon_{ii}$ are the diagonal elements of the strain tensor. In the presence of hydrostatic pressure and biaxial stress, $\varepsilon_{ii}$ can be decomposed into $\varepsilon_{ii} = \varepsilon_{ii}^{(h)} + \varepsilon_{ii}^{(b)}$. $\varepsilon_{ii}^{(h)}$ is the hydrostatic strain, which has the form

$$\varepsilon_{xx}^{(h)} = \varepsilon_{yy}^{(h)} = \varepsilon_{zz}^{(h)} = -\frac{P}{C_{11}^{Ge}+2C_{12}^{Ge}} \tag{4}$$

where $C_{11}^{Ge}$ and $C_{12}^{Ge}$ are the elastic constants for Ge, and P is the applied hydrostatic pressure. The biaxial strain in the Ge layers is

$$\varepsilon_{xx}^{(b)} = \varepsilon_{yy}^{(b)} = \frac{a^{Si}(P) - a^{Ge}(P)}{a^{Ge}(P)}$$

$$= \frac{a_o^{Si} - a_o^{Ge}}{a_o^{Ge}} + \frac{a_o^{Si}}{a_o^{Ge}}\left[ \frac{1}{C_{11}^{Ge}+2C_{12}^{Ge}} - \frac{1}{C_{11}^{Si}+2C_{12}^{Si}} \right] P \tag{5}$$

where a(P) is the lattice constant at pressure P and $a_o$ is the lattice constant at ambient pressure. Also

$$\varepsilon_{zz}^{(b)} = -\frac{2C_{12}^{Ge}}{C_{11}^{Ge}}\,\varepsilon_{xx}^{(b)} \tag{6}$$

Inserting Eqs. (4) - (6) into Eq. (3) gives

$$\Delta\omega_{strain} = \frac{1}{\omega_0}\left( q - p\,\frac{C_{12}^{Ge}}{C_{11}^{Ge}} \right)\left( \frac{a_o^{Si}}{a_o^{Ge}} - 1 \right) \tag{7}$$

which is the usual lattice mismatch correction due to the compressive strain in Ge layers at ambient pressure, which gives the +15.8 $cm^{-1}$ contribution mentioned earlier, and

$$\delta\omega_{strain}(P) = -\frac{p+2q}{2\omega_0(C_{11}^{Ge}+2C_{12}^{Ge})}\,P$$

$$+ \frac{1}{\omega_0}\frac{a_o^{Si}}{a_o^{Ge}}\left( q - p\,\frac{C_{12}^{Ge}}{C_{11}^{Ge}} \right)\left[ \frac{1}{C_{11}^{Ge}+2C_{12}^{Ge}} - \frac{1}{C_{11}^{Si}+2C_{12}^{Si}} \right] P \tag{8}$$

The first term is due to hydrostatic pressure applied to bulk Ge. The second term is due to the change in Ge and Si lattice constants with pressure because Ge and Si have different compressibilities; this results in a decrease in compressive strain in Ge layers with increasing pressure.

The Effect of Confinement

At ambient pressure, the confined Ge modes for an n-atom layer are at frequencies $\omega_c^{(m)}$, which are obtained approximately by zone folding the bulk LO dispersion curve at $k^{(m)} = m\pi/nd_0$,[7] where $d_0$ is the monolayer spacing and $m = 1,2,\cdots n$. The $m = 1$ mode corresponds to the principal confined mode, which is at $0.5(2\pi/a)$ for the Ge layers of the SLS, where $a = 4d_0$ is the lattice constant. Consequently, $\omega_0$ should replaced by $\omega_c^{(1)}(k = \pi/a)$. Since the Grüneisen parameter $\gamma$ varies across the bulk LO phonon dispersion curve, the pressure-dependent "bulk" contribution, which is the first term on the right hand side in Eq. (8), will be different for each confined mode. Using the notation introduced earlier, the changes in phonon frequency and Grüneisen parameter for a given confined mode can be treated as leading to perturbations from the $k = 0$ Raman shifts. Calculations suggest that $\gamma$ for LO phonons decreases by ~ 0.044 [11] or ~ 0.059 [12] as k increases from 0 to $\pi/a$ along (001) in Ge. Since the principal confined mode in the Ge layers is at $\pi/a$, the difference in $d\omega/dP$ between $k = \pi/a$ and $k = 0$ is estimated to be

$$\delta\omega_{confinement}(P) = 3P(\gamma\Delta\omega_{confinement}+\omega_0\Delta\gamma_{confinement})/(C_{11}^{Ge}+2C_{12}^{Ge})$$

$$= \begin{cases} -0.028\ P \quad cm^{-1}\ (\text{for } \Delta\gamma = -0.044) \\ -0.034\ P \quad cm^{-1}\ (\text{for } \Delta\gamma = -0.059) \end{cases} \tag{9}$$

where $\Delta\omega_{confinement} = -9.0\ cm^{-1}$ and P is in kbar. With $\gamma = -(p+2q)/6\omega_0^2$, p and q at $k = \pi/a$ can be obtained assuming either that p, q, and $\gamma$ change proportionately from $k = 0$ to $\pi/a$ or that $(p-q)/2\omega_0^2 = 0.23$, as for c-Ge.[10] In either case, it is seen that the effect of confinement on the second term in Eq. (8) is negligible.

Using the parameters in Refs. 10 and 13 for Si and Ge, $d\omega/dP$ for principal confined Ge mode in the Si/Ge SLS, and the zone center optic phonons in c-Ge and c-Si are expected to be 0.314, 0.355 and 0.481 $cm^{-1}$/kbar, respectively, excluding confinement effects. From Eq. (8), the effect of strain in the Ge layers is expected to decrease $d\omega/dP$ by 0.041 $cm^{-1}$/kbar relative to c-Ge. Inclusion of the confinement effect using the first estimated value in Eq. (9) decreases the expected value of $d\omega/dP$ in the Ge layers of the SLS to 0.286 $cm^{-1}$/kbar, which is 0.069 $cm^{-1}$/kbar lower than the c-Ge value. The second value in Eq. (9) gives $d\omega/dP$ that is 0.075 $cm^{-1}$/kbar lower. Our corresponding experimental values are $0.31 \pm 0.03$, $0.37 \pm 0.02$ and $0.49 \pm 0.02$ $cm^{-1}$/kbar for the SLS Ge, c-Ge and c-Si. This experiment shows that the effects of strain and confinement decrease $d\omega/dP$ in the Ge layers by 0.06 $cm^{-1}$/kbar relative to that in c-Ge, which is within experimental error of the prediction. Our measured $d\omega/dP$ values for c-Si and c-Ge are in agreement with the values obtained using p and q, and with previously measured values $0.52 \pm 0.03$ $cm^{-1}$/kbar for c-Si [14] and $0.385 \pm 0.005$ $cm^{-1}$/kbar for c-Ge,[15] which included a $P^2$ term in analyzing $\omega(P)$. Including this $P^2$ term in our analysis brings our $d\omega/dP$ values even closer to those in Refs. 14 and 15.

As applied pressure is increased to the limit of 62.5 kbar applied here, Eq. 5 shows that the biaxial strain in the Ge layers decreases from ~4.0% to ~3.3%. If the pressure were increased to the maximum possible before a phase transition occurs (P ~ 110 kbar), phase transitions occur at ~ 110 and ~ 125 kbar in Ge [15] and Si [14] respectively, the biaxial strain in Ge decreases to ~ 2.8% and remains compressive. As is true for Si/Ge structures, it is also generally found for other SLS's that the superlattice layer with the larger lattice constant is also the more compressible. Therefore the magnitude of biaxial strain initially decreases with pressure and, as in Si/Ge SLS's, the structure becomes more stable. In some structures, compressive layers will eventually become tensile with added pressure (and vice versa) and eventually they will become larger than the critical thickness and misfit dislocations will form.

In conclusion, the difference between $d\omega/dP$ for the principal quasi-confined LO mode in Ge layers in a Si/Ge SLS and that in bulk c-Ge can be explained by biaxial strain and confinement. The perturbation on $d\omega/dP$ for Ge due to confinement is comparable in magnitude and has the same sign as that due to strain. In contrast, confinement and strain lead to perturbations of roughly comparable magnitudes but opposite signs in the Raman frequency measurement at ambient pressure for the SLS studied here. With improved precision, the Grüneisen parameter for Si and Ge LO phonons from the $\Gamma$ to the X point can be determined from Raman measurements of $d\omega/dP$ in $Si_nGe_m$ SLS's on the [001] substrates for different n and m. Similarly, $\gamma$ for LO and TO phonons propagating in other directions can be obtained using SLS's grown on substrates with different crystal orientations and the proper Raman polarization selection rules. This method can be used to determine the Grüneisen parameter for optical phonons with arbitrary wavevector in any bulk material by analyzing confined phonons in ultrathin layers of this material.

ACKNOWLEDGMENTS

This work was supported at Columbia by the Joint Services Electronics Program Contract DAAL 03-91-C-0016 and by the Office of Naval Research. The authors would like to thank Judah A. Tuchman for his valuable advice and assistance regarding diamond anvil cell technique.

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