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Symmetrically strained Si/Ge superlattices on Si substrates

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Symmetrically strained Si/Ge superlattices with an overall thickness of 0.2 μm, well above the critical thickness ($\approx$ 10 nm) of unsymmetrically strained superlattices of the same composition, are studied. Strain adjustment is obtained by growing thin homogeneous $Si_{0.4}Ge_{0.6}$ buffer layers (20 nm) on Si substrates. The period lengths vary in the range 0.7–2.8 nm. Raman scattering experiments confirm quantitatively the strain distribution and the superlattice periodicity. Observed zone-folded acoustic-phonon energies agree well with theoretically expected dispersion relations.

Strained-layer superlattice (SLS's) made of ultrathin Si and Ge layers are predicted to modify essentially the properties of Si-like materials with indirect electronic band gaps.[1,2] Recently, the first interesting experimental results on new optical transitions were published on Si/Ge SLS's grown on (100) Si (Ref. 3) (electroreflectance) and (110) Ge substrates[4] (photoluminescence).

The very important class of Si-based Si/Si_xGe_{1-x} heterostructures[5,6] and superlattice devices promises monolithic integration with conventional integrated circuits. However, ultrathin Si/Ge SLS's on Si substrates with equidistant layers can only be grown up to a critical thickness less than 10 nm.[3] The unsymmetrical strain distribution (Si unstrained, Ge fully strained) yields to an energetic instability. On the other hand, symmetrically strained SLS's are stable up to an unlimited overall thickness.[7]

In the present Rapid Communication we report on the growth of ultrathin Si/Ge SLS's on Si substrates with an overall thickness much larger than obtainable in unsymmetrically strained counterparts. Further, we report on strain symmetrization by incorporation of a thin homogeneous buffer layer. Strain distribution and superlattice periodicity are verified by Raman scattering experiments. We observe characteristic shifts in optical-phonon frequencies and zone-folded acoustic doublet modes. Inelastic light scattering has been used as a versatile tool for studies of semiconductor heterostructures and superlattices made of Si and Ge.[8]

The Si/Ge SLS's were grown in a Si molecular-beam epitaxy (MBE) apparatus which is commonly used for homoepitaxial device work.[9] For the present experiments an additional pyrolytic boron nitride (PBN) effusion cell for Ge evaporation was provided. The growth rate was about 1 nm/min. Superlattice formation proceeded at a substrate temperature of 350 °C by opening and closing the respective source shutters. Opening and closing times ware chosen to adjust the ratio of Ge and Si layer thickness (in monolayers, ML) as 2:3. A schematic of the structures grown is shown in Fig. 1. The SLS period lengths $d = d_{Si} + d_{Ge}$ were varied from 5 ML (0.69 nm) to 20 ML (2.76 nm). 1 ML corresponds to 6.56×10^{14} atoms/cm^2. The number of periods was chosen between 73 and 290 in order to obtain a SLS overall thickness h_{SL} of about 0.2 μm, a much higher value than the critical thickness of unsymmetrically strained Si/Ge SLS's of the same composition. The SLS's are covered by 1 nm Si caps to protect the structure from oxidizing after removal from the MBE apparatus. The (100) Si substrates were chemically precleaned (oxidizing etch followed by a HF dip), *in situ* annealed at 900 °C for 5 min, and covered by a thin (20 nm) Si layer with MBE at 550 °C. The essential strain adjustment in the superlattice layers was achieved by growth of a thin (20 nm) homogeneous $Si_{1-y}Ge_y$ buffer layer on the cleaned substrate at 450 °C. For SLS's the stability criterion[7] requires strain adjustment to $\varepsilon_{Si} d_{Si} + \varepsilon_{Ge} d_{Ge} = 0$, where ε_{Si} and ε_{Ge} are the lateral strain components in Si and Ge, respectively. $Si_{1-y}Ge_y$ buffer and Si substrate can be considered as a virtual substrate with an effective Ge content y^* which

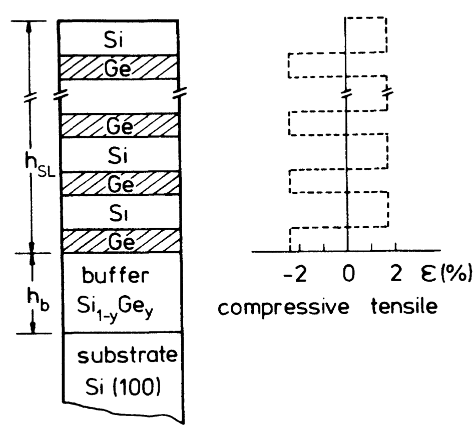

FIG. 1. Schematic diagrams showing the SLS's and the strain field in the commensurate layers. The strained buffer contains a misfit dislocation network.

provides a new in-plane lattice constant to the following superlattice. Design of the virtual substrate,[10] dislocation structure,[5,7] and metastability regimes[11] of heteroepitaxy have been already reported.

In order to get strain symmetrization in the Si/Ge layered system with thickness ratio of 3:2 we used a 20-nm-thick $Si_{0.4}Ge_{0.6}$ buffer layer which corresponds to an effective Ge content $y^* = 0.4$ with a lateral lattice constant $a_b = 5.52$ Å. We expect a strain distribution inside the superlattice layers $\varepsilon = (a_b - a_{S0})/a_0 = -2.4\%$ (Ge) and about $+1.7\%$ (Si). The total strain field of the SLS is shown by a dashed line in the right part of Fig. 1. It is oscillating around $\varepsilon_{av} = (\varepsilon_{Si} d_{Si} + \varepsilon_{Ge} d_{Ge})/(d_{Si} + d_{Ge}) = 0$ necessary to grow SLS's without limitation in the overall thickness h_{SL}.

The actually strain distributions in our samples are measured by Raman scattering. Figure 2 shows a phonon spectrum of the sample (12/8), i.e. (12 ML Si)/(8 ML Ge), at room temperature. The penetration depth of the used laser light is smaller than h_{SL} and therefore information is only obtained from the superlattice layers. In the wave-number range of optical phonons two strong and sharp lines appear at $\omega_0 = 306$ and 506 cm^{-1} close to the first-order Raman signals of pure Ge ($\omega_0 = 300$ cm^{-1}) and pure Si ($\omega_0 = 520$ cm^{-1}), marked by dashed lines. The wave numbers of these modes shift linearly with stress according to Ref. 12.

Due to the biaxial stress in pseudomorphic SLS's (30 kbar in Si) the optical phonon is expected at $\omega_{Si} = 508$ cm^{-1} marked by an arrow in Fig. 2. In Ge the stress has opposite direction (-34 kbar) yielding to a positive shift in energy. From the calculation it follows $\omega_{Ge} = 312$ cm^{-1} also marked by an arrow.

For both phonons there are small shifts of experimental frequencies (Table I) to lower values with respect to calculated energies. This shift is more pronounced for optical vibrations in the smaller period Si/Ge SLS's indicating a confinement of optical modes.

The spectrum in Fig. 2 shows besides the strain-shifted optical modes a much weaker phonon signal close to 406 cm^{-1}. It corresponds to Si-Ge vibrations well known from Raman spectra of Si_xGe_{1-x} alloy crystals. In our case we attribute this to a small amount of interface roughening or disorder.

In addition to the optical modes several strong lines from folded acoustic phonons (doublet modes) appear in the low-energy region of the SLS spectrum in Fig. 2 not observed in bulk materials. It was demonstrated by Lockwood and co-workers[13] and Brugger *et al.*[14] that the dispersion of folded acoustic modes in Si_xGe_{1-x} SLS's is well described by the layered elastic continuum model. The inset in Fig. 2 shows a small part of the $\omega(q)$-characteristic for La (solid lines) and TA modes (dashed lines) based on such calculations. Only the section around the first folded doublets ($|m| = 1$) close to the Brillouin zone center is drawn. We assign the two strong lines in Fig. 2 to the first folded LA doublet ($m = \pm 1$). The satellite peak is close to the $m = -1$ position of the first folded TA phonon. Also the next-higher-order peak of

TABLE I. Phonon wave numbers of symmetrically strained Si/Ge superlattices expressed in units of cm^{-1}.

Sample (ML Si)/(ML Ge)	ω_{Si}	ω_{Ge}	$\omega_{Si/Ge}$	ω_{LA} ($m = \pm 1$, mean value)
12/8	506	306	406	74
6/4	506	298	413	162
3/2	502	292	410	...

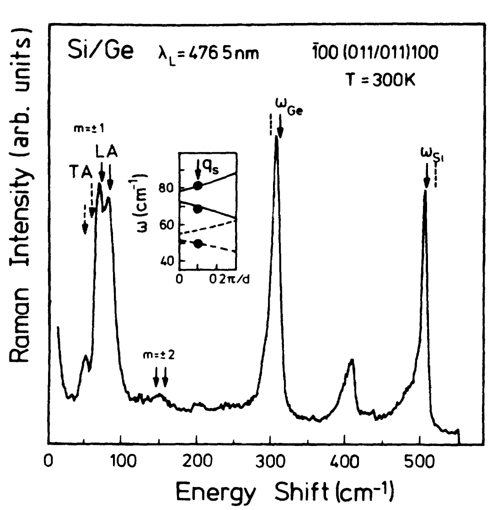

FIG. 2. Raman spectrum of a Si/Ge SLS with 12 ML Si and 8 ML Ge. The inset shows the calculated dispersion of acoustic phonons.

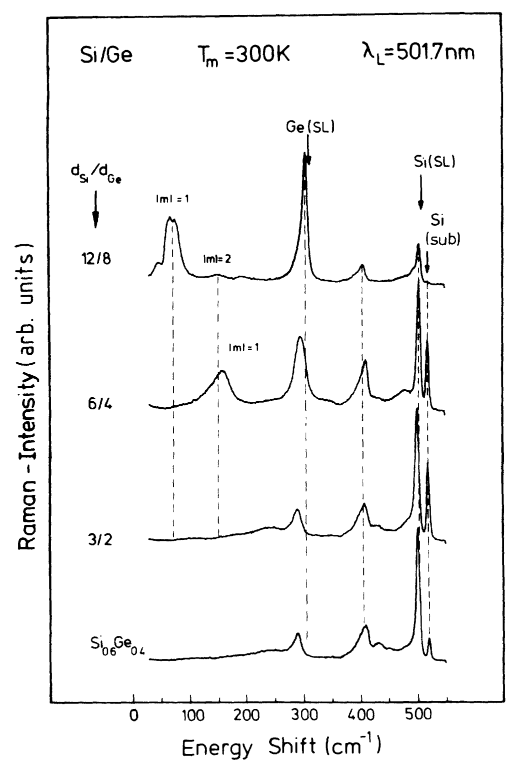

FIG. 3. Phonon spectra of SLS's with various period lengths. For comparison a spectrum of a SiGe alloy on a Si substrate is also shown.

LA with $|m|=2$ appears much weaker around 150 cm^{-1}. The experimental data are in excellent agreement with a period length $d=12$ ML Si+8 ML Ge as intended from growth conditions.

Figure 3 shows Raman spectra of three Si/Ge SLS's with $d_{Si}/d_{Ge}=3{:}2$ but period lengths d of 20, 10, and 5 ML. The samples were grown under same conditions as discussed above. An additional spectrum of a 0.4-μm-thick alloy layer grown on a similar substrate is also plotted in the figure. The total thickness of SLS's is $h_{SL}=0.2$ μm for all samples. It was measured by a mechanical surface stylus at the film edges and agreed with the predicted value within $\pm 1\%$. All spectra in Fig. 3 are taken with the 501.7-nm line of an Ar^+ laser. Therefore the phonon spectra of sample (12/8) differs from that in Fig. 2 which was measured with $\lambda_L=476.5$ nm. Especially the intensity variation of optical phonons demonstrate the different resonance behavior in Si and Ge layers. This effect is much less pronounced in samples with smaller period lengths indicating a change of the electronic band structure from individual Si and Ge layers to a superlattice. For smaller periods, however, the Si phonon and the Si-Ge mode are gaining intensity compared to the Ge mode.

A second interesting feature is the intensity of the Si substrate phonon at 520 cm^{-1}. Although all three SLS samples have the same thickness, the substrate phonon is much more pronounced in the smaller period samples (10 ML, 5 ML). They are more transparent in the green spectral range. The absorption coefficient increases with period length in otherwise identical superlattices. The observed change in optical properties is evidence for an altered electronic band structure.

In the acoustic frequency range the first LA doublet ($|m|=1$) of sample (6/4) appears at the same energy as the second LA doublet of sample (12/8) as expected from the doubled period length. The doublet splitting is, however, not resolved anymore. The phonon spectra of sample (3/2) is already similar to that of the corresponding alloy. This tendency is expected by considering finite interface roughness together with ultrathin layers.

In summary, phonon Raman scattering was used to demonstrate the first successful growth of thick superlattices which consist of pure Si and pure Ge layers. This was achieved by incorporation of an appropriate buffer layer yielding to a symmetrical strain distribution in the layers directly probed by optical phonon energy shifts. The observation of folded acoustic modes confirmed the period length of the multilayer structure.

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