PHYSICAL REVIEW B VOLUME 53, NUMBER 11 15 MARCH 1996-I

Phonon strain-shift coefficients of $Si_{1-x}Ge_x$ grown on Ge(001)

M. Stoehr, D. Aubel, S. Juillaguet, J. L. Bischoff, L. Kubler, and D. Bolmont
Laboratoire de Physique et de Spectroscopie Electronique, URA 1435, Faculté des Sciences et Techniques, Université de Haute-Alsace, 4 rue des Frères Lumière, 68093 Mulhouse, France

F. Hamdani
Max Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Federal Republic of Germany

B. Fraisse and R. Fourcade
Laboratoire des Agrégats Moléculaires et des Matériaux Inorganiques, Université Montpellier II, Place E. Bataillon, 34095 Montpellier Cedex 5, France

(Received 11 October 1995)

High germanium content $Si_{1-x}Ge_x$ alloys have been grown pseudomorphically at 400 °C on Ge (001) by molecular-beam epitaxy. The germanium fraction determined using x-ray diffraction measurements ($x=0.8$) is in good agreement with the value obtained with *in situ* x-ray photoemission results and vapor flux control. Combining Raman spectroscopy results and the epilayer stress value obtained by x-ray diffraction, we have determined the strain-shift coefficient (b) for each main Raman line (Ge-Ge, Si-Ge, and Si-Si). The variation of b is similar to the Grüneisen parameter (γ) alloy variation, i.e., b and γ values increase with increasing chemical disorder. The use of Raman scattering as a direct tool to determine the strain is discussed. The temperature dependence of the phonon frequencies has also been studied in the range from 300–5 K.

I. INTRODUCTION

Built-in strains play a crucial role in tailoring optical and electronic properties of thin films and superlattices.[1] SiGe-based heterostructures can be grown with huge strain within the epitaxial layers because of the 4% lattice mismatch between Si and Ge. In the development of growth methods for high-quality $Si_{1-x}Ge_x$-based structures, as, for example, strained superlattices grown on totally relaxed SiGe buffer layers, more information on the stress at all stages of the growth in the various layers is necessary. Silicon technology is nowadays so dominant that most of the work devoted to strain determinations in $Si_{1-x}Ge_x$ layers concerns growth on silicon substrates.[1–6] These pseudomorphic $Si_{1-x}Ge_x$ epilayers are under a biaxial compressive strain in the plane parallel to the interface, in the whole germanium concentration range. However, the growth of alternate $Si_{1-x}Ge_x$ layers with different germanium concentration on a $Si_{1-y}Ge_y$ buffer layer leads to a biaxial tensile strain in the $Si_{1-x}Ge_x$ epilayer for $y>x$. In order to obtain more information on this particular state of strain we have investigated high germanium content $Si_{1-x}Ge_x$ alloys grown on germanium substrates.

In this work we report on the characterization of high germanium content $Si_{1-x}Ge_x$ epilayers grown on Ge. We have performed *in situ* measurements such as low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), and x-ray photoelectron diffraction (XPD) on the epilayer either to ascertain its crystallographic structure or to determine its germanium concentration. *Ex situ* x-ray diffraction measurements confirm these results and allow the determination of the strain. Raman spectroscopy has been performed in the temperature range from 300 to 5 K in order to obtain the variation with temperature of the frequency of the three main alloy phonon modes (Ge-Ge, Si-Ge, and Si-Si). From the x-ray diffraction and Raman spectroscopy results at room temperature, we deduce the strain-shift coefficients for the main phonon lines. Such coefficients for different germanium concentrations are essential for calculating the strain present in each layer which forms $Si_{1-x}Ge_x/Si_{1-z}Ge_z$ superlattices when they are analyzed by Raman spectroscopy. The phonon strain-shift coefficient determined on $Si_{1-x}Ge_x$ layers grown on Si (Refs. 4 and 5) reveals an alloy dependence.[4] The value given by Cerdeira *et al.*[5] for $x<0.65$ is two times lower than the value given by Lockwood and Baribeau[4] for $x<0.35$. Other recent works[3] have reported, using the strain shift of the Si-Si phonon, a lower relaxation factor on SiGe/Si grown by APCVD (atmospheric pressure chemical vapor deposition), compared to previous work on SiGe/Si grown by molecular-beam epitaxy (MBE).[1] We determine in this paper strain-shift coefficients in high-Ge-content SiGe/Ge and point out the alloy variation of these coefficients with the composition. Our study shows that the low strain relaxation factor[3] previously determined is just an artifact resulting from the use of underestimated b values.

II. EXPERIMENT

A high-germanium-concentration $Si_{1-x}Ge_x$ alloy was grown at 400 °C on a (001) Ge substrate in a MBE equipment previously described.[6] Before growth, the substrate is cleaned *in situ* by Ar^+ sputtering cycles followed by annealing at 700 °C. This procedure generates a Ge(001) 2×1 reconstructed surface as observed by the corresponding LEED pattern. During growth the silicon and the germanium fluxes were stabilized by keeping the temperature of the evaporation cells constant. The flux calibration is obtained using a

0163-1829/96/53(11)/6923(4)/$10.00

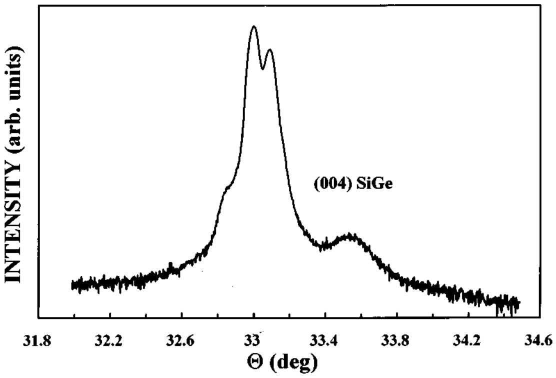

FIG. 1. X-ray diffraction spectrum of a 20-nm $Si_{1-x}Ge_x$ alloy ($x=0.8$) grown on Ge(001) obtained with the Cu $K\alpha$ radiation. The diffraction line intensity is shown on a logarithmic scale. The diffraction lines at lower angle than 33.4° are due to the germanium substrate.

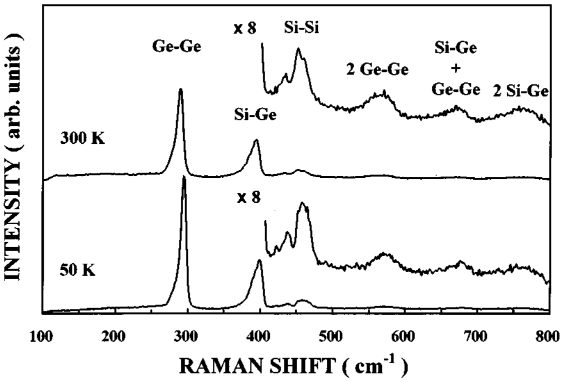

FIG. 2. Raman spectra of a 20-nm $Si_{1-x}Ge_x$ alloy ($x=0.8$) grown on Ge(001) recorded at 300 and 50 K with the 488-nm Ar^+ laser line.

quartz monitor, giving an estimate of the germanium concentration in the alloy of 80±2%.

X-ray diffraction measurements with Cu $K\alpha$ radiation were used to determine the germanium content and estimate the stress in the epilayer. The accuracy of the x-ray measurements ($\Delta d/d$) is estimated to be 2×10^{-3} (d is the distance between the observed planes). The Raman spectra were recorded at different temperatures between 300 and 5 K in a backscattering geometry using a DILOR triple-grating spectrometer and a charge-coupled device multichannel detector. The excitation wavelengths were 514.5 and 488 nm from an Ar^+ laser with a typical power level of 20 mW on 0.5 mm^2. Angular-resolved XPS analyses allow the structural characterization, as more extensively explained in a previous report.[6]

III. RESULTS AND DISCUSSION

The similarity of the x-ray photoelectron diffraction patterns obtained by polar scans of the Si $2p$ and Ge $3d$ core-level intensities indicates the same structural order in the epilayer and in the substrate and hence epitaxial growth. This is also confirmed by the 2×1 reconstructed LEED pattern obtained.

The lattice parameter of the corresponding bulk SiGe with the same germanium concentration content is 0.5608 nm.[7] The lattice mismatch between the epilayer ($a_{\rm epi}$) and the substrate ($a_{\rm sub}$) material is given by $\varepsilon_{xx}=(a_{\rm sub}-a_{\rm epi})/a_{\rm epi}=(8.7\pm0.5)\times10^{-3}$. The critical thickness below which pseudomorphic growth can be maintained for this mismatch should be about 200 nm;[8] in our case the layer thickness is 20 nm, thus the epilayer is assumed to be completely strained. The low growth temperature (400 °C) allows us to neglect the thermal strain that arises from the difference in the thermal expansion coefficient[7] between the germanium substrate and the $Si_{1-x}Ge_x$ layer. Using elasticity theory and a linear variation of the compliance constants S_{ij} with alloy composition, the tensile stress on the $Si_{1-x}Ge_x$ layer is given by $\sigma=\varepsilon_{xx}/(S_{11}+S_{12})=1.3\pm0.1$ GPa. Figure 1 shows an x-ray diffraction spectrum of a 20-nm-thick $Si_{1-x}Ge_x$ layer grown on Ge(001), with the intensity given in a logarithmic scale. Two main diffraction lines observed at $\theta=33.00\pm0.02°$ and $33.08\pm0.02°$ are attributed to the Cu $K\alpha1$ and $K\alpha2$ (004) Ge reflections from the substrate. The position of the Cu $K\alpha1$ (004) $Si_{1-x}Ge_x$ reflection is determined at $\theta=33.53\pm0.03°$. A direct use of the Bragg law provided a SiGe lattice parameter perpendicular to the interface of 0.5577±0.0043 nm. The strain (ε_{zz}) in the growth direction is related to the in-plane mismatch (ε_{xx}) by

$$\varepsilon_{zz}=\frac{2S_{12}}{S_{11}+S_{12}}\,\varepsilon_{xx}\,. \tag{1}$$

Using Eq. (1), we determine the lattice parameter of a relaxed alloy, with the same Ge content to be 0.5609±0.0043 nm, corresponding to $x=0.80\pm0.01$. Owing to the strain parallel to the interface and the elastic constants of this $Si_{1-x}Ge_x$ alloy, a tensile stress value of 1.3±0.1 GPa is obtained in this layer, which is in close agreement with the value estimated above for a pseudomorphic layer.

The Raman spectra of the 20-nm $Si_{0.2}Ge_{0.8}$ layer presented in Fig. 2 show four lines between 200 and 500 cm^{-1} and three above 500 cm^{-1}. Three of the lines below 500 cm^{-1} are strong; they are related to Ge-Ge, Si-Ge, and Si-Si vibrations. At 300 K, they are observed at 289.1±0.2, 393.6 ±0.2, and 455.2±0.2 cm^{-1}, respectively. All these lines are asymmetric to low frequencies, as expected for a random alloy.[9] A weak structure at 436 cm^{-1} is also observed; it has been discussed earlier.[10] Similar Raman modes have already been obtained on $Si_{1-x}Ge_x$ single crystals.[9–17] The three lines at 567, 762, and 672 cm^{-1} correspond respectively to the 2(Ge-Ge), 2(Si-Ge) and (SiGe+GeGe) overtones. We point out that these second-order modes peak at frequencies lower than twice the first-order values (Si-Ge and Ge-Ge) or the addition of these two frequency modes; a difference varying from 14 to 28 cm^{-1} is observed. Analogous second-order peaks as well as their shifts with respect to the corresponding sums of first-order frequencies, were observed by Lannin[11] in high germanium content SiGe crystals. To distinguish between the Raman lines arising from the substrate and those from the epilayer, we have analyzed a germanium substrate under the same experimental conditions. As presented in Fig. 3, the germanium substrate provides, in the frequency range from 200 to 1000 cm^{-1}, two main lines at 301 and 578 cm^{-1} associated, respectively, with Ge-Ge vibration and its overtone. We conclude that the lines at 289

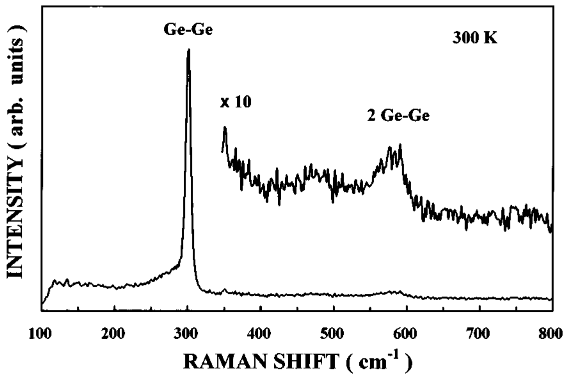

FIG. 3. Raman spectrum of a germanium substrate recorded at 300 K with the 488-nm Ar^+ laser line.

and 567 cm^{-1} observed in Fig. 2 arise only from the epilayer; the fact that no substrate modes appear on Fig. 2 indicates that the energy of the laser line used is in resonance with the electronic level $(E_1+\Delta_1)$ of the SiGe epilayer.[8] We notice that all Raman line frequencies depend on germanium content, stress, and temperature.

The biaxial strain splits the triply degenerate optical phonon mode at the Brillouin center into a singlet with vibrational eigenvectors parallel to the strain axis, and a doublet with eigenvectors perpendicular to that axis.[18] In a backscattering geometry and with [001] growth direction, only the singlet is observed and the phonon frequency shift $\delta\omega=(\omega-\omega_0)$ is given by[5]

$$\delta\omega=\frac{1}{2\omega_0}\left[\frac{2S_{12}}{(S_{11}+S_{12})}\,p+2q\right]\varepsilon_{xx}=b\varepsilon_{xx}, \qquad (2)$$

where ω_0 is the bulk phonon frequency, p and q are phenomenological parameters describing the anharmonicity of the spring constants, and b is the phonon strain-shift coefficient for a [001] shear strain. To obtain a more precise determination of the strain-phonon shift, we have measured both Stokes and anti-Stokes phonon shifts. We also measured the alloy dependence of the phonon frequencies for bulk $Si_{1-x}Ge_x$ single crystals under the same experimental conditions. We obtain strain-induced frequency shifts $\delta\omega_{\text{Si-Si}}=-9.0\pm0.4$ cm^{-1}, $\delta\omega_{\text{Si-Ge}}=-7.7\pm0.4$ cm^{-1} and $\delta\omega_{\text{Ge-Ge}}=-6.2\pm0.4$ cm^{-1}. We note that $\delta\omega$ is negative for the three main phonon modes, thus confirming that the epilayer is under biaxial tensile strain. Taking $\varepsilon_{xx}=(8.6\pm0.5)\times10^{-3}$, we obtain the b values for the first-order phonon modes, given in Table I. As shown in Table I, the strain-shift coefficients of the Si-Ge vibration are higher than strain-shift coefficients in both c-Si and c-Ge. On the other hand the strain-shift coefficients of both Si-Si and Ge-Ge phonons increase with alloy disorder. The b-alloy dependence is in accordance with previous hydrostatic pressure studies;[14,15] the Grüneisen parameter $\gamma=-[(p+2q)/6\omega_0^2]$ reported in Table I shows also an increase with alloy disorder that was interpreted by an increase of Brillouin zone-edge contribution to the first-order phonon peaks with increasing alloy disorder.[15] It is worth noting that γ is usually larger at the zone boundaries than at the zone center in c-Si and c-Ge and the phonon density of state presents a maximum at the zone boundaries. The phenomenological parameters p and q can be determined only by the observation of singlet-doublet phonons splitting. The doublet phonons are allowed in the configuration where the light wave vector is normal to the crystal growth axis and with crossed polarizations of scattered and incident light. Cerdeira *et al.*[5] have determined $b=-455$ cm^{-1} for Si-Ge vibration, this value is two times lower than the values reported in this paper. The underestimated value of b given by Ref. 5 can be explained by the use of noncompletely relaxed samples as reference for no shift phonon frequencies (ω_0) instead of well-known bulk values, on the other hand, stress values had not been determined by x-ray measurements. In Ref. 3 the authors have used the Si-Si phonon shift to determine the strain relaxation factor in SiGe/Si. As shown in Table I, the strain-shift coefficient of the Si-Si vibration depends on alloy concentration. On the other hand, the value used in these works is taken from Cerdeira *et al.*,[5] which underestimates the b values. By taking a correct value of b it turns out that the strain relaxation factors in APCVD-grown SiGe/Si are quite similar to those obtained previously in MBE-grown SiGe/Si.[1]

Raman measurements at temperature down to 5 K were performed on the same sample. At 5 K, using the 541.5-nm excitation wavelength, both Ge-Ge Raman lines from the layer and the substrate are observed with a frequency difference of 8 cm^{-1}. Below 50 K, an additional weak structure appears at 422 cm^{-1}. These additional peaks, between 400 and 500 cm^{-1}, have been attributed by Alonso and Winer[10] to the localized Si-Si motion in the neighborhood of one or more Ge atoms. Lockwood *et al.*[16] have claimed that these

TABLE I. Phonon strain-shift coefficients (b) and mode Grüneisen constants (γ) in $Si_{1-x}Ge_x$.

		$Si_{1-x}Ge_x$				
		$x=0$	$x=0.2$	$x=0.35$	$x=0.8$	$x=1$
b (cm^{-1})	Si-Si	-723 ± 50[a]	-850 ± 50[a]	-950 ± 50[a]	-1052 ± 120[b]	
	Si-Ge		-710 ± 50[a]	-990 ± 50[a]	-895 ± 100[b]	
	Ge-Ge		-810 ± 50[a]	-925 ± 50[a]	-728 ± 100[b]	-408 ± 50[a]
γ[c]	Si-Si	1.0 ± 0.1	1.1 ± 0.1	1.2 ± 0.1	1.4 ± 0.1	
	Si-Ge		1.2 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	
	Ge-Ge		1.3 ± 0.1	1.3 ± 0.1	1.16 ± 0.1	1.12 ± 0.1

[a] Reference 4.
[b] Present work.
[c] Reference 14.

peaks give evidence of long-range ordering in strained epitaxial layers SiGe/Si. We agree with the first interpretation since we have observed those additional lines even in bulk $Si_{1-x}Ge_x$ with similar germanium content. As the temperature decreases, the peak intensities and the peak position frequencies increase while the full widths at half maximum decrease. The Raman linewidths obtained for $Si_{0.2}Ge_{0.8}$/Ge are close to those obtained for the corresponding bulk $Si_{0.2}Ge_{0.8}$, indicating the absence of a broadening due to strain inhomogeneities in the epilayer. The intensity ratio between the main phonon peaks and their corresponding overtones increases with decreasing temperature. The frequency shift of the main Raman line with temperature, in the range from 50 to 300 K, is estimated to be -0.02 cm^{-1}/K, in good agreement with values previously observed on polycrystalline $Si_{1-x}Ge_x$ alloys in the temperature range from 300 to 900 K.[17]

IV. CONCLUSION

In conclusion, high-germanium-content $Si_{1-x}Ge_x$ epilayers were pseudomorphically grown on a Ge(001) substrate and characterized using x-ray diffraction and Raman spectroscopy. Strain-shift coefficients of the phonons lines are determined using both x-ray diffraction and Raman spectroscopy. These values are in accordance with those given by Lockwood and Baribeau[4] for $x<0.35$ and higher than the c-Ge and c-Si values. The increase of phonon strain-shift coefficients in $Si_{1-x}Ge_x$ may result from the relaxation of momentum conservation in a disordered alloy. Further investigations on the origin of b-alloy increase are under study.

ACKNOWLEDGMENTS

We are very grateful to M. Cardona for helpful and stimulating discussions, and for supplying bulk $Si_{1-x}Ge_x$ samples. F.H. acknowledges the support of the Alexander von Humboldt Foundation. Thanks are due to S. Jandl and X. J. Zhou for help with Raman measurements and to N. Esser for a critical reading of the manuscript.

---

[1] T. P. Pearsall, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, San Diego, 1991), Vol. 33, p. 223.

[2] N. L. Rowell, J. P. Noel, D. C. Houghton, and M. Buchanan, Appl. Phys. Lett. **48**, 963 (1991).

[3] C. H. Perry, F. Lu, and F. Namavar, Solid State Commun. **88**, 613 (1993); F. Lu, C. H. Perry, F. Navamar, N. L. Rowell, and R. A. Soref, Appl. Phys. Lett. **63**, 1243 (1993).

[4] D. J. Lockwood and J. M. Baribeau, Phys. Rev. B **45**, 8565 (1992).

[5] F. Cerdeira, A. Pinczuk, L. C. Bean, B. Batlogg, and B. A. Wilson, Appl. Phys. Lett. **45**, 1138 (1984).

[6] D. Aubel, M. Diani, M. Stoehr, J. L. Bischoff, L. Kubler, D. Bolmont, B. Fraisse, R. Fourcade, and D. Muller, J. Phys. (France) III **4**, 733 (1994).

[7] J. P. Dismukes, L. Ekstrom, and R. J. Paff, J. Phys. Chem. **68**, 3021 (1964).

[8] T. P. Pearsall, F. H. Pollak, J. C. Bean, and R. Hull, Phys. Rev. B **33**, 6821 (1986).

[9] W. J. Brya, Solid State Commun. **12**, 253 (1973).

[10] M. I. Alonso and K. Winer, Phys. Rev. B **39**, 10 056 (1989).

[11] J. S. Lannin, Phys. Rev. B **16**, 1510 (1977).

[12] D. W. Feldman, M. Ashkin, and J. H. Parker, Phys. Rev. Lett. **17**, 1209 (1966).

[13] M. A. Renucci, J. B. Renucci, and M. Cardona, in *Light Scattering in Solids*, edited by M. Balanski (Flammarion, Paris, 1971), p. 326.

[14] Z. Sui, H. H. Burke, and I. P. Herman, Phys. Rev. B **48**, 2162 (1993).

[15] J. B. Renucci, M. A. Renucci, and M. Cardona, Solid State Commun. **9**, 1651 (1971).

[16] D. J. Lockwood, K. Rajan, E. W. Fenton, J.-M. Baribeau, and M. W. Denhoff, Solid State Commun. **61**, 465 (1987).

[17] H. H. Burke and I. P. Herman, Phys. Rev. B **48**, 15 016 (1993).

[18] F. Cerdeira, C. J. Buchenauer, F. H. Pollak, and M. Cardona, Phys. Rev. B **5**, 580 (1972).