Composition and strain in thin $\text{Si}_{1-x}\text{Ge}_x$ virtual substrates measured by micro-Raman spectroscopy and x-ray diffraction

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Micro-Raman spectroscopy was employed for the determination of the germanium content, x and strain, ϵ , in ultrathin SiGe virtual substrates grown directly on Si by molecular beam epitaxy. The growth of highly relaxed SiGe layers was achieved by the introduction of point defects at a very low temperature during the initial stage of growth. SiGe virtual substrates with thicknesses in the range 40–200 nm with a high Ge content (up to 50%) and degree of relaxation, r , in the range 20%–100% were investigated using micro-Raman spectroscopy and x-ray diffraction (XRD) techniques. The Ge content, x , and strain, ϵ , were estimated from equations describing Si–Si, Si–Ge, and Ge–Ge Raman vibrational modes, modified in this study for application to thin SiGe layers. The alteration of the experimentally derived equations from previous studies was performed using independent data for x and r obtained from XRD reciprocal space maps. A number of samples consisting of a strained-silicon (s-Si) layer deposited on a SiGe virtual substrate were also analyzed. The stress value for the s-Si varied from 0.54 to 2.75 GPa, depending on the Ge-content in the virtual substrates. These results are in good agreement with theoretically predicted values. © 2011 American Institute of Physics. [doi:10.1063/1.3536508]

I. INTRODUCTION

Virtual substrates intended to be applied as global strain platforms for n-metal-oxide-semiconductor field-effect transistors (MOSFETs) consist of standard Si wafers with epitaxially overgrown SiGe buffer layers. In SiGe buffer layers, a high Ge content and a high degree of relaxation are essential because they provide the required strain in the Si channel as a quantum well for electrons. Strain relaxed buffers (SRB) are preferred to be thin for improved heat dissipation in MOSFETs, for better compatibility with devices of low dimensions in integrated circuits, as well as for lower time and energy consumption during their production. Naturally, the quality of virtual substrates is very critical for the performance of the final device. The SRB must have a smooth surface morphology and low defect density. Lattice mismatch between Si and SiGe causes strain relaxation by the introduction of misfit dislocations in the interface plane and, especially, undesired threading dislocations in the bulk of the layers. The latter can be reduced by special additional measures connected mostly with the growth of much thicker graded or constant composition layers, or with additional ex situ treatment.^{1–4} Thus, SRB with small thickness, high Ge content, and high degree of relaxation is a rather ambitious aim. In order to lattice match SiGe buffer layers with the Si substrate, a controlled introduction of point defects at the beginning of SiGe buffer epitaxial growth, below the critical thickness, was proposed in Refs. 5 and 6. This can be realized by extreme reduction in growth temperature or by *in*

situ bombardment with Si^+ ions available in the molecular beam epitaxy (MBE) chamber during the solid source MBE (first stage of growth).⁷ During the next epitaxy stage at a medium growth temperature of typically 550 °C, high point defect concentration should lead to the formation of prismatic dislocation loops (instead of dislocation arms threading through the whole layers), and so promote the early relaxation and lower threading dislocation density. The degree of relaxation can be adjusted by the choice of the very low temperature (VLT) step.

The industrial and research developments require metrology solutions for the characterization and subsequent control of several important parameters in SiGe/Si and Si/SiGe/Si structures such as the type and the magnitude of strain in the s-Si layer as well as the Ge content (x) and relaxation factor (r) in the SiGe buffers. Raman spectroscopy and x-ray diffraction (XRD) are the only techniques which facilitate obtaining all the aforementioned parameters simultaneously. We note that other techniques, which can be also used for the determination of x value, are Rutherford backscattering spectrometry (RBS) and secondary ion mass spectrometry (SIMS). However, RBS is not very accurate for measurements of thin films in a complicated structure, while SIMS is a destructive technique. XRD is quite accurate technique (in particular, when using advanced equipment with high resolution), but it requires a longer measurement time and is rarely utilized for in-line sample measurements. Therefore, the investigation of the application of Raman spectroscopy for accurate measurements of SiGe virtual substrates is of great importance.

Raman spectroscopy was applied widely for the investi-

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gation of composition and stress in Si/Ge structures such as SiGe epitaxial layers,^{8–14} Si/Ge superlattices,^{15–18} and Ge/Si quantum wells and quantum dots.^{19,20} For these structures the Ge content, x and strain, ε (or r) can be obtained using three different methods of Raman data analysis. These are: (i) frequency method, using a set of the experimental equations obtained for the peak positions of the Si–Si, Si–Ge, and Ge–Ge modes, (ii) intensity method, using the ratio of the integrated intensities of above mentioned modes, and finally (iii) using thin Si-cap layer (or strained-silicon layer, s-Si), deposited on top of the SiGe, layer along with coherence conditions for these two layers. We note, that Raman investigations were applied in the past to the analysis of composition and strain of bulk SiGe,^{9,10} as well as to samples deposited by different variations in the chemical-vapor deposition (CVD) techniques (e.g., Ref. 8) and liquid-phase epitaxy.¹¹ Quite recently micro-Raman technique was applied to samples deposited by reduced pressure CVD (Ref. 12) and plasma enhanced CVD.^{13,14} However, a very small number of works were devoted to micro-Raman investigation of samples deposited by the MBE technique (see Refs. 15–23), and most of these works were dealing with Si/Ge superlattices and quantum dots.^{17–23} It is worth noting that majority of the investigated SiGe samples had a thickness in the range from 300 to 4000 nm, and in addition to that these layers were deposited on top of step-graded or gradually graded $\text{Si}_{1-x}\text{Ge}_x$ buffer with x varied from 0 to the required value of x .

The main purpose of this work is to investigate the application of micro-Raman spectroscopy to very thin SiGe virtual substrates grown by the MBE technique. We also evaluate the validity of the existing equations, obtained for Raman data analysis, with the application to thin SiGe virtual substrates using independent evaluation of the Ge content and strain from XRD data. Based on the results of the independent XRD measurements we first analyzed the set of equations for all three modes for fully relaxed samples. Taking into account the contribution of strain to the shift in the phonon modes in SiGe layer the adjusted set of equations for the analysis of Raman data registered for any virtual SiGe substrate in the range of $0 < x < 0.5$ was obtained. This enabled us to use micro-Raman spectroscopy for the analysis of MBE grown, thin, virtual SiGe substrates, with a maximal deviation in the absolute value for Ge content, x , of ± 0.04 , relative to XRD data. In addition to this, the strained Si layers grown on SiGe buffers were also investigated.

II. EXPERIMENTAL

A. Sample growth

For the growth of virtual substrates with ultrathin (< 100 nm) SiGe buffer layers of high Ge content, a method using point defect supersaturation by a two-step growth procedure in an MBE system is employed.^{5,6} The first stage at a VLT (135–150 °C) serves for the generation of point defects and their supersaturation in the growing layer. During the second stage, growth of an equal composition layer continues at a conventional MBE temperature of 550 °C. Here, point defects accumulated at the VLT stage may condense

FIG. 1. (Color online) Schematic of (a) SiGe virtual substrate and (b) of a strained-Si layer on an ultrathin SiGe buffer including a buried part with point defect supersaturation at low temperature initiating the early relaxation.

and form dislocation loops which support the early relaxation. Interaction of point defects with dislocations introduced during plastic strain relaxation can also improve the layer quality.²⁴

Numerous samples, schematically shown in Fig. 1(a), are grown for the investigation of thin SiGe virtual substrates with Ge content ranging from 10 to $\sim 50\%$ as well as strained Si grown on top of some of these virtual substrates [Fig. 1(b)]. The epitaxial layers are grown with a solid source Si MBE equipment for 150 mm substrates.²⁵ Si was evaporated from an electron beam evaporator and Ge from a special effusion cell.²⁶ The total thickness of the investigated SiGe buffer layer varies from 40 to 80 nm, including the VLT parts with thickness ranging from 20 nm to 30 nm, respectively (see Ref. 6 for details). For s-Si samples, above the SiGe buffer layer, a SiGe intermediate layer is grown which, among others things, may serve for quantum well doping and for spacer formation. In these series of samples, Ge content in the intermediate layers is the same as that of the SiGe buffer layer. The total thickness of the buffer layer combined with the intermediate layer does not exceed 200 nm. A 10–20 nm thick strained-Si layer is obtained at 500 °C under conditions providing coherent growth of pseudomorphic layers (sample parameters are given in Table I).

B. Raman measurements and analysis

1. Raman measurements

Unpolarized Raman spectra were registered at room temperature in backscattering geometry using a RENISHAW 1000 micro-Raman system equipped with a Leica microscope. Some additional measurements were also performed in Renishaw using a Micro-Raman inVia System. Data was registered at excitation wavelengths of Ar^+ ion laser at 514.5,

TABLE I. Nominal thickness and composition for samples with s-Si on SiGe virtual substrate [related to structures from Fig. 1(b)].

Sample name	Thickness of s-Si (nm)	SiGe layer composition
1797	20	$\text{Si}_{0.88}\text{Ge}_{0.12}$
1669	15	$\text{Si}_{0.8}\text{Ge}_{0.2}$
1799	12	$\text{Si}_{0.7}\text{Ge}_{0.3}$
1800	8	$\text{Si}_{0.6}\text{Ge}_{0.4}$

488, and 457 nm and a 325 nm HeCd laser with inVia system for investigation of samples with s-Si. The thin SiGe layers are penetrated by visible light producing a Si substrate peak which is useful for calibration but also demands careful line analysis for extraction of nearby lines from SiGe. Laser light was focused on the sample through the $\times 50$ magnification microscope objectives that provide a laser spot size in the range $\sim 1\text{--}3\ \mu\text{m}$. The scattered light from the sample was collected through the same microscope and directed through a spectrometer. It was then detected with a charge-coupled device. The laser power was kept between 3 and 10 mW to prevent samples heating and as a result causing an unwanted peak position shift. Before undertaking measurements the influence of laser power on the linewidth and the peak position were checked on one of the samples from the series; the power was chosen at a level which did not affect the aforementioned spectra parameters. For the majority of samples, the data were collected at three to five different locations on the sample and no significant variance was observed, with average values well within experimental error limits.

Raman spectra registered from numerous samples, with x and r varying from 0.1–0.5 and 20%–100%, respectively, were analyzed in order to accurately determine the peak position, peak intensity and the linewidth of the phonon modes. RENISHAW WIRE software allows Raman peaks to be fitted with a variety of inbuilt functions for different peak shapes. To determine the Ge content and strain from the set of equations for Si–Si, Si–Ge, and Ge–Ge vibrational modes (as described in Sec. III A), the position of these peaks must be measured with a high accuracy. Two factors enable us to do so. A position of a Si–Si peak from the Si substrate was used as an internal reference for thin SiGe layers for visible excitation and a position of plasma line for UV excitation. All peaks from the SiGe layer were fitted with asymmetrical function,²⁷ while Si–Si peaks for s-Si and Si substrate were fitted by a Lorentzian function or by a mixture of Lorentzian and Gaussian functions.

2. Determination of peak position from experimental Raman spectrum

The major source of uncertainty in using frequency shifts to determine the composition and strain of a $\text{Si}_{1-x}\text{Ge}_x$ buffer layers stems from the difficulty of accurately measuring the peak positions for Si–Si, Si–Ge, and Ge–Ge phonon modes. This is due to their asymmetry, large linewidth and small intensity, particularly for $x < 0.3$.

For analysis of all three peaks associated with the SiGe layer an asymmetrical function was implemented [see Eq. (1)] into a user defined functions in ORIGIN. This allowed a better estimate to be made of the half width at half maximum (HWHM) of the spectrum, the intensity and the wave number of an asymmetrical peak from the following equation:²⁷

FIG. 2. (Color online) Fitting of Ge–Ge band with asymmetrical [Eq. (1)] and Gaussian functions. The example of the best choice for I_{bkl} and I_{bkr} points used in Eq. (1) is also shown.

$$\begin{aligned}
 I(\omega) = & \frac{1}{2} \times \frac{[1 - \text{sign}(\omega - \omega_0)] \times I_0}{\left(\frac{\omega - \omega_0}{W_1}\right)^2 + 1} + \frac{1}{2} \\
 & \times \frac{[1 - \text{sign}(\omega_0 - \omega)] \times I_0}{\left(\frac{\omega_0 - \omega}{W_2}\right)^2 + 1} + \frac{1}{2} \\
 & \times [1 - \text{sign}(\omega - \omega_0)] \times I_{bkl} + \frac{1}{2} \\
 & \times [1 - \text{sign}(\omega_0 - \omega)] \times I_{bkr}, \quad (1)
 \end{aligned}$$

where ω_0 is the peak position, I_0 is the peak intensity, W is the HWHM at the lower frequency side (W_1) and at the higher frequency side (W_2) of the spectrum, I_{bkl} is the background intensity on the lower frequency side of the curve, and I_{bkr} is the background intensity on the higher frequency side of the curve (see Fig. 2). The function $\text{sign}(\omega - \omega_0)$ turns to -1 if $(\omega - \omega_0)$ is negative and 1 if $(\omega - \omega_0)$ is positive. Analysis of the peak positions proved to be considerably more accurate after the addition of these two terms. The asymmetrical function was found to fit the data better than the single Gaussian function (see example on Fig. 2) or the set of standard Lorentzian and Gaussian functions. This was most notably in particular for the Si–Ge mode at higher Ge concentrations as the asymmetry of this band does increase with increasing Ge content. An example of choosing values for the I_{bkl} and I_{bkr} points used in Eq. (1) is shown in Fig. 2, in order to best fit the Si–Ge band obtained from a particular example at $x=0.35$.

C. XRD measurements

For high resolution XRD (HRXRD) measurements the BRUKER D8 Discovery with a primary beam channel cut Ge (110) crystal monochromator, producing an intense, parallel $\text{Cu } K\alpha_1$ monochromatic beam (with wavelength $\lambda = 1.5406\ \text{\AA}$), was used. The secondary beam was equipped with a LynxEye 1D detector allowing for fast mapping of the reciprocal space. The sample lattice parameters were determined by measuring reciprocal space maps (RSMs) around the Si [113] reflection and estimating the thin film lattice

FIG. 3. (Color online) (a) Raman spectra for SiGe/Si samples with $r > 90\%$ and different Ge content. (b) Raman spectra for strained SiGe/Si samples with different Ge content.

parameters from the relative separation in Ω and 2θ . For sample 940 RSMs were also registered around Si [224] reflection; the obtained results were similar to Si [113] reflection. Strain and Ge concentration were then obtained by assuming the lattice expansion due to the Ge content obeying Dismukes²⁸ model.

III. RESULTS AND DISCUSSIONS

A. Frequency method

1. Equations for fully relaxed SiGe layers

The Raman spectrum of a strained SiGe heterostructure alloy consists of three distinct peaks whose energies (and therefore the peak positions) depend on the x (Ge content) and the strain.^{9,10,18} The three strong first-order lines shown in Fig. 3 in Raman spectra of a few SiGe virtual substrates are due to the atomic vibrations of Si-Si (at ~ 502 cm⁻¹), Si-Ge (at ~ 405 cm⁻¹) and Ge-Ge (at ~ 290 cm⁻¹) bonds in the SiGe alloy. The Raman spectra for SiGe virtual substrates with different Ge content and with nearly the same high relaxation factor ($r > 93\%$), i.e., for fully relaxed samples, are presented in Fig. 3(a). It can be seen from this figure that the position of all three peaks are shifted with respect to each other depending on x .

The spectra obtained for samples with different composition and relaxation factor (or strain), shown in Fig. 3(b), demonstrate a quite substantial shift in all three modes from their position for fully relaxed samples. As can be seen from Fig. 3(b) the position of all three bands is changed depending on x and ε . The values of x and ε can be estimated from a set

of equations suggested in the literature for bulk SiGe or relatively thick SiGe layers grown by the CVD technique. This includes the bulk materials, obtained by powder compression,¹⁰ single crystal SiGe alloy grown by liquid-phase epitaxy¹¹ as well as SiGe layers deposited by different CVD methods of deposition on graded SiGe layers or directly onto a Si substrate. For the Si-Si peak position, ω_{SS} , of a SiGe layer the following experimental equations are introduced

$$\omega_{SS}(x) = 520 - 70x \quad [11], \quad (2a)$$

$$\omega_{SS}(x) = 520.2 - 62x \quad [8, 10], \quad (2b)$$

$$\omega_{SS}(x) = 521.2 - 67.9x \quad [19], \quad (2c)$$

$$\omega_{SS}(x) = 520.7 - 66.9x \quad [14]. \quad (2d)$$

Equations (2a)–(2c) are valid mainly in the region of Ge content $0 < x < 0.5$, while Eq. (2d) is obtained for the wide range of x . The following equations are used for Si-Ge peak position, ω_{SG}

$$\omega_{SG} = 400.5 + 14.2x \quad [8], \quad (3a)$$

$$\omega_{SG} = 400.5 + 12x \quad [11], \quad (3b)$$

in the range of $0 < x < 0.5$ and for $0 < x < 1$ the following expressions are used

$$\omega_{SG} = 400 + 22.07x - 36.14x^2 + 83.73x^3 - 88.54x^4 \quad [19], \quad (3c)$$

$$\omega_{SG} = 400.1 + 24.5x - 4.5x^2 - 33.5x^3 \quad [14]. \quad (3d)$$

The experimentally measured dependences of the Ge-Ge phonon frequency, ω_{GG} , on x are described by the equations

$$\omega_{GG} = 282.5 + 16x \quad [8], \quad (4a)$$

$$\omega_{GG} = 280.8 + 19.37x \quad [17], \quad (4b)$$

$$\omega_{GG} = 280.3 + 19.4x \quad [14]. \quad (4c)$$

In order to determine the optimal set of expressions suitable for our samples we select a number of samples with different Ge content and with relaxation factor close to 100%. The Ge content for these samples is obtained by XRD and the Raman peak position is corrected for the small residual strain determined from the relaxation degree (Table II)

$$\varepsilon = -f(1 - r), \quad (5)$$

with ε as a strain, f as a lattice mismatch, and r as a strain relaxation. Strain and mismatch have different signs as compressive strain is defined as negative in elasticity theory. f is a parabolic function of the Ge content, x , when slight deviation from Vegard's law (linear interpolation between Si and Ge) is taken into account as given by Dismukes²⁸ for the bulk SiGe. This equation was confirmed later for epitaxial layers²⁹

TABLE II. The calculated Ge concentration and relaxation factor for samples measured by XRD and Raman techniques [related to structures from Fig. 1(a)].

Samples	Ge content, x (mole fraction)				Relaxation factor r (%)		
	HRXRD	Frequency method Eq. (11)	Intensity method		HRXRD	Raman, r_1	Raman, r_2
			Eq. (16) $A=1.7$	Eq. (17) $B=3$			
753	0.22	0.23	0.22	0.25	81.7	95	95
759	0.22	0.23	0.23	0.22	24.5	28	21
746	0.26	0.27	0.29	0.28	93	97	97
940	0.29	0.31	0.19	0.29	23	33	26
937	0.32	0.29	0.20	0.35	68	86	85
936	0.35	0.32	0.34	0.42	77	80	78
1303	0.36	0.39	0.31	0.37	16	26	19
938	0.37	0.33	0.20	0.33	85	61	58
1308	0.37	0.39	0.37	0.40	104	104	104
775	0.43	0.40	0.41	0.41	83	93.5	93
774	0.44	0.41	0.45	0.44	92	99	98
776	0.44	0.40	0.43	0.41	95	93	93
773	0.45	0.42	0.44	0.39	99	98	97
1027	0.46	0.43	0.46	0.44	79	81	80

$$f(\text{SiGe}) = \frac{0.02}{0.5431}x + \frac{0.0026}{0.5431}x^2. \quad (6)$$

The relaxation degree r of the selected samples varies between 92% and 104%. The values larger than 1 stem from a small tensile strain originating from thermal mismatch of completely relaxed SiGe layers cooled down to room temperature. The correction of the Raman peak position for strain is performed using the literature values^{8,30–32} of strain phonon coefficients -830 cm^{-1} , -575 cm^{-1} , and -384 cm^{-1} for Si–Si, Si–Ge, and Ge–Ge bands, respectively. The accurate values of these literature strain-phonon coefficients are not critical, because of the only small correction needed for the selected samples. The results are shown in Fig. 4.

2. Equations for fully relaxed SiGe layers

The peak position obtained for all three Raman modes after the fitting with asymmetrical function are plotted in Fig. 4 against values of x , determined from XRD measurements. The linear curves obtained from Eqs. (2a)–(2d) on the dependence of Si–Si peak position versus Ge content are shown in Fig. 4(a) together with Raman and XRD experimental data. The same set of data and linear and nonlinear dependences are shown in Fig. 4(b) for Si–Ge and in Fig. 4(c) for Ge–Ge modes.

As can be seen from Fig. 4(a), the best fit to XRD data results in the linear equation

$$\omega_{SS} = 520 - 70.5s, \quad (7)$$

which is quite close to the equation obtained in Ref. 11, see Eq. (2a).

Figure 4(b) shows a similar set of data for peak position of Si–Ge mode versus x obtained from XRD data. In this case, the experimental data obtained for our set of samples significantly deviate from the linear and nonlinear dependen-

cies described by Eqs. (3a) and (3b) and Eqs. (3c) and (3d). The best fit to obtained experimental data results in the following linear equation for $0 < x < 0.5$:

$$\omega_{SG} = 400.5 + 16x. \quad (8)$$

As can be seen from Fig. 4(c) a significant deviation of the experimental data points from all curves is observed for the Ge–Ge peak position versus x . This confirms previously made conclusions,⁸ that it is more difficult to use the Ge–Ge peak for the extraction of information on x from Raman data, particularly for thin SiGe layers with $x < 0.4$. For consistency we will analyze our experimental results for all three peaks described above, using Eq. (4a) obtained in Ref. 8 for a Ge–Ge peak. However, most of the data analysis was done based on Eqs. (7) and (8).

3. Equations for strained SiGe layers

The next step is to determine the set of equations for strained SiGe virtual substrate with relaxation factor $< 100\%$. For this purpose, the additional terms accounting for strain in Eqs. (4a), (7), and (8) were used.⁸ This results in the following set of equations describing the peak position of SiGe layer under strain

$$\omega_{SS} = 520 - 70.5x - 830\varepsilon, \quad (9)$$

$$\omega_{SG} = 400.5 + 16x - 575\varepsilon, \quad (10)$$

$$\omega_{GG} = 282.5 + 16x - 384\varepsilon. \quad (11)$$

From Eqs. (9) and (10), we obtain the following expressions for x and ε calculations:

$$x = \frac{(\omega_{SG} - 400.5) - 0.6928 \times (\omega_{SS} - 520)}{64.84}, \quad (12)$$

FIG. 4. (Color online) (a) Si-Si, (b) Si-Ge, and (c) Ge-Ge Raman peak position vs Ge content determined by HRXRD.

$$\varepsilon_{\text{SiGe}} = \frac{520 - \omega_{\text{SS}} - 70.5x}{830}. \quad (13)$$

The results of calculations of x and ε using Eqs. (12) and (13) enable us to process the Raman data obtained for the numerous samples investigated in this work, with x in the range 0 to 0.5 and for the relaxation factor in the range 20%–100%.

The following relationships, describing the shift in the peak positions for all three modes for fully strained layers, were obtained based on Eqs. (9)–(11) and assuming for simplicity a linear relationship (Vegard's law) between Ge content and strain:

$$\Delta\omega_{\text{SS}} = 36x, \quad \Delta\omega_{\text{SG}} = 40x, \quad \text{and} \quad \Delta\omega_{\text{GG}} = 32x. \quad (14)$$

The degree of relaxation, r in a SiGe layer on a Si substrate can be obtained using the experimental Raman shift in the

FIG. 5. Raman shift in (a) Si-Si, (b) Si-Ge, and (c) Ge-Ge peak as a function of Ge content. Dotted lines correspond to the dependence of $\Delta\omega$ vs Ge content for fully strained samples and dashed line for fully relaxed samples.

Si-Si peak $\Delta\omega_{\text{exp}}$ from the unstrained peak position for a Si substrate at 520 cm^{-1} from the following expression:^{15,33}

$$r_1 = \frac{\Delta_{\text{exp}} - \Delta_s}{\Delta_r - \Delta_s} \times 100\%, \quad (15)$$

where $\Delta_r = 70.5x$ and $\Delta_s = 36x$ are Raman shifts in the fully relaxed and the fully strained epilayers from the bulk Si, respectively. In addition, the r values were also calculated from the expression (5) and these are denoted as r_2 in Table II.

The results, shown in Figs. 5(a)–5(c), demonstrate distribution of the obtained data between two linear dependencies of phonon frequencies versus x , obtained for the fully strained and fully relaxed SiGe virtual substrates. It can be

FIG. 6. (Color online) Deviation of Ge content obtained from Raman and XRD data ($x_{\text{Raman}} - x_{\text{HRXRD}}$) vs Ge content determined by HRXRD measurements.

seen that the obtained data are within the range of data possible for different values of x for the investigated samples. A small deviation of experimental data from the fully strained curve for Ge-Ge mode is observed; this is due to the difficulties of Ge-Ge peak analysis for samples with small Ge content. The results of comparing data obtained from XRD and Raman techniques for the relaxation factor and Ge content are summarized in Table II. We can see that the deviation of the values obtained by Raman spectroscopy for the relaxation factor for some samples, for example for samples 940, 937, and 938, is larger than that obtained for the x value (this will be discussed in Sec. III B). Figure 6 demonstrates the difference between the x values obtained from Raman (x_{Raman}) and XRD (x_{XRD}) measurements versus Ge content. We can see that the maximal deviation of x values estimated from Raman data are within ± 0.04 relatively to XRD data. Bearing in mind the difficulties with analysis of data for very thin layers we believe that the obtained results demonstrate the usefulness of micro-Raman spectroscopy for the determination of Ge content and strain (or degree of relaxation) in thin SiGe layers.

B. Intensity method

Let us now analyze the second approach for the determination of composition in SiGe alloy using Raman spectroscopy. The methods suggested in Refs. 8, 9, and 34 are based on the comparison of the relative intensities of the first order Si-Si, Si-Ge, and Ge-Ge bands. The ratios of the integrated intensities of three main modes can be related in the first-order approximation to the number of nearest neighbor bonds and, therefore, are the functions of the Ge content in the alloy. According to a simple statistical model, the relative intensities are roughly proportional to the relative numbers of corresponding bonds types, i.e., $(1-x)^2$, x^2 , and $2x(1-x)$ for the Si-Si, Ge-Ge, and Si-Ge modes, respectively.⁹

The major advantage of using the intensity method is that there is no need for highly accurate fitting of the phonon bands, which is extremely important for the frequency method described in Sec. III A 3. The determination of alloy composition using the intensity of the modes is also independent of whether the layer is strained or relaxed. However, the

FIG. 7. The various baselines that can be chosen in calculating the intensities of the Si-Si, Si-Ge, and Ge-Ge modes. The black dashed line indicates the baselines used in this work.

intensities of the Si-Ge and Ge-Ge modes depend strongly on the methods used to measure them. In particular, there is some uncertainty about the determination of the baseline for each particular band shown in Fig. 7. This problem is especially pertinent for the Si-Ge mode as there are significant peaks on the high energy side of the main mode. These have been attributed to localized Si-Si motion in the neighborhood of one or more Ge atoms.^{9,10,18} As was stated in Ref. 34, the localized Si-Si peaks were included in the measurement of integrated intensity of the Si-Ge mode. In this investigation, the intensity of the Si-Ge mode was measured excluding the peaks at 430 and ~ 450 cm^{-1} and the area of the Ge-Ge peak was estimated by excluding the long wings on both sides of the curve (see black dashed baseline in Fig. 7). The intensity of Si-Si mode was measured by fitting a single peak from SiGe layer (truncated in the wave number region as shown in Fig. 7) when this peak is well separated from Si-Si peak of Si substrate. If two Si-Si peaks were in close proximity, the simultaneous fitting of both peaks was performed with mixture of Lorentzian and Gaussian functions.

Assuming random mixing in the alloy, the relative integrated intensities of the modes are expected to vary with the Ge mole fraction as follows:³⁴

$$\frac{I(\text{Si-Si})}{I(\text{Si-Ge})} = \frac{A(1-x)}{2x} \quad (16)$$

$$\text{and } \frac{I(\text{Ge-Ge})}{I(\text{Si-Ge})} = \frac{Bx}{2(1-x)}. \quad (17)$$

Because of resonance effects, the intensities of the various modes vary with the wavelength of the exciting light, as does the optical system. Thus, coefficients A and B must be determined experimentally for each wavelength. A and B were determined for our experimental setup for 457 nm excitation wavelength using the XRD data available for a number of samples as described above.

The integrated intensities of phonon modes were calculated by using the RENISHAW WIRE peak profile analysis software. Using x values, measured by XRD, the relative intensities for the investigated samples are plotted versus Ge content in Figs. 8(a) and 8(b). As can be seen from both figures the best fitting of experimental data is obtained at A

FIG. 8. Intensities ratio vs Ge content, x from the experimental data (symbols) and (a) from Eq. (16) at $A=1.85$ (gray line) and $A=1.7$ (black line) and (b) from Eq. (17) at $B=3.2$ (gray line) and $B=3$ (black line).

$=1.7$ and $B=3.0$. By comparing Figs. 8(a) and 8(b), it seems that better correlation between Raman and XRD results is achieved with Eq. (16). This is not surprising bearing in mind that the Ge-Ge peak for a thin SiGe layer is quite weak, in particular for small x .

As can be seen from Table II, the intensity method enables the determination of x to an accuracy of ± 0.05 using Eq. (16). As was mentioned above, considerable uncertainty exists as to where the baseline of a peak begins and where it ends. Mooney *et al.*³⁴ found the integrated intensities ratios to be in good agreement with Eqs. (16) and (17) only if the peak at 430 cm^{-1} is included in the intensity of the Si-Ge mode, while in this work all local Si-Si peaks were excluded from the calculation of $I_{\text{Si-Ge}}$ and $I_{\text{Si-Si}}$. When these peaks were included, the accuracy of the estimation of x was reduced to ± 0.08 . Interestingly, for the samples 940, 937, and 938 described in Sec. III A 3 a significant deviation between x values obtained by XRD and from Raman intensity method using Eq. (16) was obtained. However, using Eq. (17) the results obtained for x are quite close to the XRD data. In order to allow explanation of this observation, further experimental investigations are necessary.

C. Strained Si on SiGe virtual substrate

The main feature of the Raman spectra of strained-Si on ultrathin SiGe substrates obtained with visible excitation light is the presence of three Si-Si peaks in the region $\sim 530\text{--}490\text{ cm}^{-1}$ (see Figs. 9 and 10). These are the peak at

FIG. 9. (Color online) (a) Raman spectra of sample 1797, 1669, 1799, and 1800 with increasing Ge content collected at 514 nm excitation wavelength. The strained-Si peak is observed between the Si substrate peak at 520 cm^{-1} and the Si-Si band from the SiGe layer. (b) Fitting of Raman spectrum for sample 1797 with three Lorentzian functions.

520 cm^{-1} , which corresponds to the Si substrate, the peak at $\sim 510\text{--}518\text{ cm}^{-1}$ which is assigned to strained Si and the peak in the range $\sim 490\text{--}510\text{ cm}^{-1}$ which belongs to the Si-Si mode in the SiGe layer. Depending on the Ge content and strain in the underlying SiGe virtual substrate, these three peaks can be either quite well separated or very close together. This situation is quite different from the case of Raman spectra of strained Si on thick SiGe substrates where the peak at 520 cm^{-1} is not observed due to the limited depth of laser light penetration into the SiGe layer.^{15,35} In this case the Si-Si peak arising from the Si substrate can be used with high accuracy as an internal reference in analyzing the Raman spectrum. The intensity of a peak at 520 cm^{-1} is much larger compared to the two other Si-Si peaks in the case of a thin s-Si layer on an ultrathin SiGe layer and, in particular, in comparison with the peak for s-Si, due to its small thickness [see Fig. 1(b)]. This requires very careful analysis of the Raman spectra in the range $490\text{--}530\text{ cm}^{-1}$.³⁶ Raman spectra for the four samples, registered at 514.5 nm excitation, are shown in Fig. 9(a). For the sample 1797 with low Ge content ($\sim 10\%$) there is no visible sign of the Si-Si peak from s-Si, while for the samples with higher Ge content, a small shoulder or small bump related to this peak can be seen in between the two peaks at 520 and at

FIG. 10. (Color online) Raman spectra for samples 1797, 1669, and 1799 collected at (a) 488 nm excitation and (b) at 325 nm excitation wavelength.

~490–512 cm⁻¹. By fitting the Raman spectrum with three Lorentzian functions, all three peaks are revealed as shown, for example, in Fig. 9(b). The results obtained for the shift, $\Delta\omega$, of Si–Si peak from the unstressed Si–Si peak at 520 cm⁻¹ for all analyzed samples are summarized in Table III along with data obtained using 488 and 325 nm excitations. For UV excitation, a simultaneous recording of the plasma line was used as the internal reference, because the Si–Si peak from the substrate does not show up in Raman spectrum for the shorter excitation wavelength. The values of Raman peak shift, $\Delta\omega$, obtained with all three excitation wavelengths are in good agreement (see Table III). The obtained results demonstrate that visible light Raman spectroscopy can be reliably used for the characterization of strained Si on ultrathin SiGe virtual substrates. However, careful fitting of the spectra is required in this case for proper data analysis.

By measuring the shift in the Raman peak position, $\Delta\omega$, obtained for the s-Si layer, the magnitude of stress, σ , and strain, ϵ , can be estimated by using a simple equation, describing the biaxial stress in a Si lattice^{30,32}

$$\sigma_{\text{Si}} = \Delta\omega/c \quad (18)$$

with $c = 4.61 \times 10^{-9} (\text{Pa} \cdot \text{cm}^{-1})$,

$$\epsilon_{\text{Si}}(\%) = \left(\frac{\Delta\omega}{b} \right) \times 100\% = \frac{a_{\text{Si}}^{\text{strain}} - a_{\text{Si}}}{a_{\text{Si}}} \times 100\%, \quad (19)$$

where b is the strain-phonon coefficient, which was taken as 830 cm⁻¹, a_{Si} and $a_{\text{Si}}^{\text{strain}}$ are the lattice constants of relaxed and strained Si, respectively. The values of σ_{Si} and ϵ_{Si} are related to the elastic constants as

$$\sigma_{\text{Si}} = \frac{E_f}{1 - \nu_f} \times \epsilon_{\text{Si}} \quad (20)$$

for biaxial stress. Here E_f is Young's modulus for the film and ν_f is Poisson's ratio of the film. Taking the values of E_f and ν_f as 130.2 GPa and 0.28, respectively,^{37,38} we conclude that the phonon coefficient ratio b/c should be $b/c = E_f/(1 - \nu_f) = 180.5$ GPa. The selected coefficients c and b obtained from the literature fit this relationship very well. The strain values thus obtained were compared with the data estimated for ϵ_{Si} from analysis of the spectral shifts in the Si–Si phonon band registered from the SiGe layers, taking into account the coherence conditions

$$a_{\text{SiGe}}^{\text{strain}} = a_{\text{Si}}^{\text{strain}}. \quad (21)$$

By analogy with the Eq. (19) and taking into account Eq. (21) and that

$$a_{\text{SiGe}}^{\text{strain}} = a_{\text{SiGe}}^{\text{rel}}(x)(1 + \epsilon_{\text{SiGe}}),$$

where $a_{\text{SiGe}}^{\text{rel}}(x)$ can be determined from Dismukes model,²⁸ we obtain

$$\epsilon_{\text{Si}}(\%) = \frac{a_{\text{SiGe}}^{\text{strain}} - a_{\text{Si}}}{a_{\text{Si}}} \times 100\%. \quad (22)$$

The results obtained for $\epsilon_{\text{Si}}(\%)$ estimated from Eqs. (19) and (22) are presented in Tables III and IV along with σ values obtained from Eq. (18). Both series of results for $\epsilon_{\text{Si}}(\%)$ show very good agreement. We believe that this agreement indicates that the results, obtained from the analysis of complicated Raman spectra in Si–Si mode region under visible excitation, allows us to obtain reliable data on stress in strained Si layers on SiGe virtual substrates. The calculations of the Ge content (x) and strain ϵ_{SiGe} were performed by means of simultaneous measurements of the ω_{SS} and ω_{SG} for the underlying SiGe layer, followed by calculations using the pair of Eqs. (12) and (13). The relaxation factor for a SiGe layer was also estimated from Eq. (15). The values x , ϵ , and

TABLE III. Shift in Si–Si peak ($\Delta\omega$), stress, and strain for s-Si layer obtained from Raman spectra at different excitation wavelengths [related to structures from Fig. 1(b)].

Sample name	Raman shift in Si–Si band, $\Delta\omega$ (cm ⁻¹)			σ [Eq. (18)] (GPa)	$\epsilon_{\text{Si}} \times 100\%$ (Eq. (19))
	514 nm	488 nm	325 nm		
1797	2.49	2.66	2.56	0.54	0.3
1669	5.3	...	...	1.13	0.63
1799	7.24	7.3	7.0	1.57	0.87
1800	12.7	12.5	12.4	2.75	1.53

TABLE IV. Ge content, relaxation factor, and strain in SiGe layers obtained from XRD and Raman measurements [related to structures from Fig. 1(b)].

Sample name	SiGe Relaxation factor, r (%)		SiGe $\epsilon_{\text{Si}} \times 100\%$		SiGe Ge content, x	
	XRD	Raman	Raman [Eq. (22)]	XRD	XRD	Raman
1797	42	58	0.28	0.22	0.13	0.12
1669	...	77	0.61	...	...	0.21
1799	67	61	0.75	0.85	0.30	0.32
1800	89	84	1.42	1.45	0.40	0.42

r determined from analysis of Raman spectra are in good agreement with XRD data.

Conversely, using the coherence conditions, the analysis of the Si–Si peak for s -Si layer enables us to independently evaluate the value of Ge content and strain in SiGe. The obtained results are in very good agreement with Raman analysis of SiGe bands, which supports the use of the modified Eqs. (9) and (10) for the simultaneous calculation of x and ϵ_{SiGe} in thin virtual SiGe substrates. This agreement also shows that the results obtained from the analysis of complicated Raman spectra in the Si–Si mode region allows us to provide reliable data on stress in strained Si layers on SiGe virtual substrates.

IV. CONCLUSION

The Ge content, x , and the relaxation factor, r , in thin SiGe layers were calculated using a set of equations for Si–Si, Si–Ge, and Ge–Ge Raman vibrational modes, adapted in this work for use with thin SiGe layers. The alterations to the equations were done using independent measurements of x and r , obtained from XRD and Raman measurements for fully relaxed SiGe virtual substrates.

It was shown that by using the ratios of the integrated intensities of Si–Si, Si–Ge, and Ge–Ge phonon modes for SiGe virtual substrates, values for x can be determined which are in reasonable agreement with XRD and Raman Frequency methods. The intensity method provides the additional advantage of allowing the use of the Ge–Ge peak for $x < 0.3$, while the more elaborate frequency method uses only the Si–Si and Si–Ge peaks. Based on the results discussed in this paper we conclude that for more reliable Raman analysis of thin SiGe layers both methods should be used.

Finally, visible micro-Raman spectroscopy is demonstrated to be a reliable tool for the characterization of composition and strain in ultrathin SiGe virtual substrates, as well as for strained Si, by careful fitting of the spectra. Although the accuracy of the XRD technique is higher ($< \pm 1\%$ for the determination of the Ge content) than Raman spectroscopy ($\pm 4\%$ – 10%), the latter technique is much faster. Raman spectroscopy also allows probing of the samples at different depths as well as in-line measurements. Finally, the method also enables local measurements to be taken from microstructured devices.

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