Analysis of boron strain compensation in silicon-germanium alloys by Raman spectroscopy

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The impact of heavy boron doping on the biaxial compressive strain in $Si_{1-x}Ge_x$ layers grown on Si has been investigated using Raman spectroscopy and theoretical calculations. It is shown that one boron atom is sufficient to compensate the strain due to approximately 6.9 Ge atoms. This effect is appreciably large for boron concentrations as low as 1%, typical for applications, which employ heavily boron doped layers. Using strain compensation, the Ge content can be substantially increased without increasing the stored strain energy. This phenomenon can be useful in applications, which require low-resistivity *p*-type strained $Si_{1-x}Ge_x$ layers with high Ge content.
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In applications, which employ heavily boron doped strained $Si_{1-x}Ge_x$ layers pseudomorphically grown on Si, one needs to be concerned about the impact of boron on the biaxial compressive strain in $Si_{1-x}Ge_x$, which impacts the material band gap. It has been well documented that addition of small carbon atoms to $Si_{1-x}Ge_x$ can lead to strain compensation resulting in a larger critical thickness for a given Ge concentration,[1] providing an additional degree of freedom in band gap engineering. It has been shown that boron, which is comparable in size to carbon, can also lead to strain compensation;[2] however, previous studies did not attempt to quantify the impact of boron on the stored strain energy for different B and Ge concentrations. This letter provides a theoretical model for boron strain compensation for the first time using the covalent radius of boron to calculate the lattice parameter of a Si–Ge–B alloy. The model is supported by measurements of the biaxial compressive strain in $Si_{1-x}Ge_x$ layers with different Ge and B concentrations using Raman spectroscopy.

In this study, we have used 150 mm (5 Ω cm) *n*-type Si wafers of (100) orientation. Windows were defined on an isolation oxide by photolithography and wet etching. *In-situ* boron doped $Si_{1-x}Ge_x$ epitaxial layers were selectively grown in these windows by ultra high vacuum rapid thermal chemical vapor deposition (UHV-RTCVD).[3] Films with Ge concentrations of 17% and 28% were grown at 550 °C and films with 50% were grown at 500 °C. Because the boron doping level in some of the epitaxial layers was as high as 2%, they will be referred to as ternary $Si_{1-x-y}Ge_xB_y$ alloys. The layer thickness was determined using atomic force microscopy by measuring the step height between the selectively grown layer and the surrounding oxide. The Raman analysis was carried out using a micro-Raman system manufactured by Dilor systems ($\lambda = 488$ nm).

Figure 1 shows a typical room temperature Raman spectrum obtained from a $Si_{1-x}Ge_x$ layer. The peaks at 400 and 500 cm^{-1} correspond to Si–Ge, and Si–Si bonds in $Si_{1-x}Ge_x$, respectively (a third Ge–Ge peak at 300 cm^{-1} is not shown for clarity).[4] The Si–Si peak follows a linear relationship with the germanium composition as given by Eq. (1), where x is the germanium concentration.[5] It has been shown that the peak positions fall between lines defined by Eq. (1) for $0 \leqslant x \leqslant 0.5$. For germanium concentrations close to the extremes of the interval, the peak positions follow Eq. (1a) but for $x \sim 0.3$ the peak positions are closer to (1b). The increase in the phonon frequencies for $x \sim 0.3$ is consistent with the fact that the lattice constant of the $Si_{1-x}Ge_x$ system deviates from its linearly extrapolated value around that concentration,

$$\omega_{\mathrm{Si-Si}} = 520.0 - 68x, \tag{1a}$$

$$\omega_{\mathrm{Si-Si}} = 520.2 - 62x. \tag{1b}$$

Germanium concentration in the epitaxial $Si_{1-x}Ge_x$ layers was measured by both Raman spectroscopy and secondary ion mass spectroscopy (SIMS) and the results are summarized in Table I. Calibration of the SIMS profiles for germanium concentration was established using a set of $Si_{1-x}Ge_x$ standards. The Ge concentration in these standards was established by Rutherford backscattering spectrometry (RBS) and by comparison analysis with another commercial analytical laboratory. Raman analysis was performed on fully

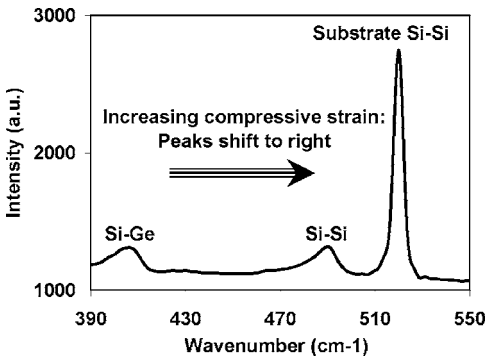

FIG. 1. Typical Raman spectrum for a boron doped $Si_{1-x}Ge_x$ film.

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TABLE I. Germanium concentration in $Si_{1-x}Ge_x$ layers determined by Raman spectroscopy and SIMS.

Si–Si peak (cm^{-1})	% Ge (Raman)	% Ge (SIMS)
487.5	47.8	45.2
502.6	28.4	27.8
509.3	17.6	17.5

relaxed $Si_{1-x}Ge_x$ layers grown above the critical thickness.[6] As shown, the two techniques are in close agreement.

Table II provides a summary of the measured Si–Ge peak positions for relaxed and strained $Si_{1-x}Ge_x$ layers with different germanium and boron concentrations. The relative strain energy in the epitaxial layers was determined by measuring the shifts of the Si–Ge peaks from their positions in relaxed $Si_{1-x}Ge_x$.[5] The thickness of the strained $Si_{1-x}Ge_x$ layers was kept well below the measured critical thickness for all the germanium concentrations studied (thickness ~25 nm). It is difficult to predict the active boron concentration in these layers due to lack of experimental data on heavily boron doped $Si_{1-x}Ge_x$ alloys. Electrical measurements using Hall effect are challenged because the Hall scattering factor changes with both Ge and B concentrations. In a previous paper, it was reported that the boron concentration levels obtained from SIMS measurements did not match those obtained from x-ray data, which could suggest that not all boron occupied substitutional sites.[2] However, in that work, the boron concentration was estimated using the lattice contraction parameter obtained from another publication for heavily boron doped Si with corrections for Ge concentration and the tetragonal distortion of the lattice. This approach could introduce estimation errors, a concern also raised in the publication. It was also mentioned that boron precipitation did not exist for boron levels as high as 2.5×10^{21} cm^{-3} but the presence of alternating B and Ge enriched layers was suggested. Due to these difficulties, in calculating the strain, we assumed that the boron atoms occupied substitutional sites. It is understood that this can be a source of error; however, we believe that the observed trend would still be valid.

The $Si_{1-x-y}Ge_xB_y$ lattice constant was determined using Vegard's law for ternary alloys[7] given by

$$a_{Si_{1-x-y}Ge_xB_y} = (1-x-y)a_{Si} + xa_{Ge} + ya_B, \tag{2}$$

where a_{Si}, a_{Ge}, and a_B are the lattice parameters of the three elements. Because boron by itself does not exist in a cubic structure like carbon, a_B was extrapolated from a plot of the known lattice constants of Si, Ge, and B versus their covalent radii. The numerical values used in this calculation as well as the estimated lattice constant for B are summarized in Table III.[8] Figure 2 shows the calculated lattice constant as a function of boron concentration for four different Ge concentrations. Using these calculated lattice parameters and assuming pseudomorphic $Si_{1-x-y}Ge_xB_y$ growth on Si, the strain in the alloy was estimated from

TABLE III. Lattice constants of Si, Ge, C, and B and their covalent radii.

Element	C	Si	Ge	B
Covalent radius	0.077	0.117	0.122	0.082
Lattice constant	3.567	5.431	5.657	3.806

$$\varepsilon = 2\frac{a_e - a_s}{a_e + a_s} \approx \frac{a_e - a_s}{a_s}, \tag{3}$$

where a_e is the lattice constant of the epitaxial layer, a_s that of the substrate, and ε is the resulting strain the layer. Assuming that there are no dislocations at the $Si_{1-x-y}Ge_xB_y/Si$ interface, the stored strain energy E_{st} can be calculated from[9]

$$E_{st} = 2\mu\varepsilon^2\frac{1+\nu}{1-\nu}t, \tag{4}$$

where t is the layer thickness, μ is the shear's modulus, and ν is Poisson's ratio. For Si and Ge, the values for μ have been calculated to be 65 and 53 GPa and the values for ν have been calculated to be 0.277 and 0.273, respectively.[10] These values have been adopted in the present calculations and linear interpolation has been used to predict values for $Si_{1-x}Ge_x$. Figure 3 shows the strain energy as a function of boron concentration for three different Ge concentrations. Solid lines represents the results of the calculations according to Eq. (4) and data points represent the values obtained from Raman spectra. It can be seen that the measurement results are in close agreement with the theoretical predictions. For fully compensated films (i.e., zero strain), the Ge:B ratio is approximately 6.9, which compares well with the ratio of 6.45 calculated by Maszara and Thompson.[11]

According to Fig. 3, boron strain compensation can be used to reduce the strain energy for a given Ge concentration. Alternatively, the same strain energy can be obtained at a higher Ge concentration by increasing the boron concentration. Consequently, thicker layers with higher Ge concentrations can be grown effectively increasing the critical thickness.

In summary, we have shown that biaxial compressive strain in $Si_{1-x}Ge_x$ alloys pseudomorphically grown on Si is reduced by boron incorporation. To fully compensate the strain, one boron atom is needed for approximately 6.9 Ge atoms. Using strain compensation, a larger critical thickness can be achieved for a given Ge concentration providing an additional degree of freedom in band gap engineering. It is

TABLE II. Si–Ge phonon peaks obtained from Raman spectroscopy.

Boron concentration (cm^{-3})	Ge=50%		Ge=28%		Ge=17%	
	Relaxed	Strained	Relaxed	Strained	Relaxed	Strained
1.00*E*+21	405.3	407.6	406.7	407.2	405.1	405.1
4.80*E*+20	405.3	408.4				
5.80*E*+19	405.3	409.3				
Undoped	405.3	409.5	406.7	408.2	405.1	405.6

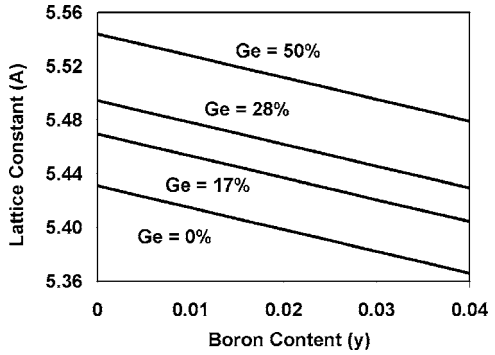

FIG. 2. $Si_{1-x-y}Ge_xB_y$ lattice constant calculated using Vegard's law.

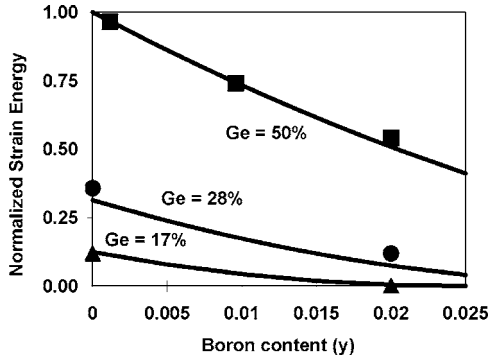

FIG. 3. Normalized strain energy as a function of boron content. The solid lines represent the theoretical calculations and the symbols represent the experimental data.

important to note that the impact of boron is appreciably large even when the boron concentration is within 1%. This is typical for applications, which employ heavily boron doped layers such as the source/drain junctions of advanced metal-oxide-semiconductor field-effect transistors (MOSFETs) with compressively strained *p*-type silicon channels and recessed $Si_{1-x}Ge_x$ junctions.[12,13]

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