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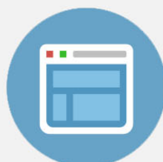
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Lattice constants and optical response of pseudomorph Si-rich SiGe:B

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Pseudomorph epitaxial films of $Si_{1-x}Ge_x$:B were grown on undoped (100) Si for $x \leq 0.026$ and the B concentration of $1.3 \times 10^{20}\,cm^{-3}$.The in-plane and out-of-plane lattice constants were determined using the X-ray techniques for 004 symmetric and 224 asymmetric diffraction. The influence of B and Ge co-doping has been detected in reflectance and ellipsometric spectra from infrared to ultraviolet. Free-hole plasma and Fano-type resonances of Si phonons and localized ^{11}B and ^{10}B vibrations have been observed. The spectral shift of E_1 electronic transitions has been quantified. We found a simple way to test the variations of Ge content using relative reflectance spectra. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4830367]

Heavily doped silicon is of interest in many branches of the semiconductor technology. The doping changes electronic and vibronic states of bulk Si; in addition, pseudomorph epitaxial layers on undoped substrates are strained due to the different radii of Si and dopants. The strain might be utilized to achieve wanted properties. On the other hand, strain compensation may be required in order to avoid the formation of dislocations or the macroscopic deformations of layered structures. Boron in Si is of particular interest owing to its large solubility. Besides others, heavy doping by B can be used as an etch stop, while the induced strain may be compensated by Ge.[1]

In this paper, we present results of X-ray diffraction and optical spectroscopy measurements of SiGe:B epilayers. We have prepared 24 silicon wafers of 630 μm thickness, 150 mm diameter, and (001) orientation. They were covered by heavily doped $Si_{1-x}Ge_x$:B epilayers with the same thickness of 3.5 μm, the same boron concentration of $1.3 \times 10^{20}\,cm^{-3}$, and 8 different values of x. The stoichiometry of SiGe was set by the germane flow during the growth, ranging from zero (no germanium) to 1.2 slm (standard liter per minute). Samples within triplets of the same x were nominally identical. The substrate temperature during the growth was 1150 °C.

Lattice parameters were measured by reciprocal space mapping using the high-resolution X-ray diffractometer with copper $K\alpha_1$ line (the wavelength of 1.54056 Å). The beam divergence was ~10 arc sec and the intensity of the primary beam was 10^6 photons/s, superposed on the laboratory background of ~1 photon/s. Reciprocal space maps in the vicinity of the symmetric 004 and asymmetric 224 lattice points were measured at two spots on each wafer. Reflectance measurements in mid-infrared (MIR) range were accomplished with vacuum FTIR spectrometer (Bruker IFS 66) at the angle of incidence of 10°. The spectral resolution was $2\,cm^{-1}$. Spectroellipsometric MIR data were collected with rotating-compensator FTIR ellipsometer (Woollam VASE-IR) at the resolution of $4\,cm^{-1}$ and several angles of incidence from 60° to 75°. The visible-ultraviolet (VIS-UV) ellipsometric data were acquired with the dispersive, rotating-compensator ellipsometer (Woolam VASE) at the angles of incidence from 65° to 85° at an equidistant (0.01 eV) photon energy mesh. The VIS-UV reflectance was measured using multichannel fibre spectrometer (Avantes 2048) with the reflectance probe consisting of the central detection fiber and 7 illumination fibers. The circular measurement spot (producing 90% of the reflected intensity) had the diameter of 300 μm.

Prior to the X-ray and optical studies, the strain due to the boron and germanium doping of the epilayer changes the curvature of the wafers. We have measured the standardized bow and warp (SEMI norms MF657 and MF534) parameters before and after the epitaxial growth, and used the difference to estimate roughly the strain. The results indicated that the lattice matching (resulting in a vanishing change of the bow and warp parameters) has been reached in our series of samples; it covers both in-plane expansion (small x) and compression (large x) of the epilayers.

The reciprocal space maps around 004 reciprocal lattice point show that the crystal lattice of the layer is not tilted with respect to the substrate for all samples. The diffraction peak originating in the epilayer shifts uniformly with the germane flow along the out-of-plane direction (Q_z). From its position, we have calculated the out-of-plane lattice constant shown in Fig. 1. The data for 0 slm (Si:B) are slightly above the best-fit linear dependence obtained from the remaining points; this indicates a tendency to a (partial) relaxation due to the large lattice mismatch of this sample. The asymmetric 224 reciprocal space maps display the position of the layer peak at the same Q_x (in-plane) values as the substrate peak for all samples within the limit $\Delta Q_x \leq 3 \times 10^{-4}\,Å^{-1}$. Consequently, the SiGe:B layers are pseudomorph with the in-plane lattice parameter differing from that of the substrate by less than 5×10^{-4} Å. The peak position along Q_z shows the same behavior as in the symmetric 004 diffraction. The lattice of the epilayer becomes cubic (unstrained) at the germane flow

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of 0.94 slm. The 1.2 slm sample displayed doublet structure of the film peak; the larger lattice constant is shown as the circled symbol in Fig. 1. Since the measurements at different spots gave the same results, we interpret it as an inhomogeneity in the growth direction.

Assuming linear dependences of the lattice constant of *unstrained* $Si_{1-x}Ge_x$:B on both B (Ref. 1) and Ge (Refs. 2 and 3) content (Vegard's law, valid for small x), we arrive at the relation,

$$a_{rl} = 5.4309(1 + 0.0367x - 5.19 \times 10^{-24} N_B)\text{Å}, \quad (1)$$

where N_B is the boron concentration in cm^{-3}. The value of a_{rl} results from the in- and out-of-plane lattice constant of the pseudomorph layer, a_{Si} and $a_{\|}$, respectively, as

$$a_{rl} = (C_{11} a_{Si} + 2C_{12} a_{\|})/(C_{11} + 2C_{12}), \quad (2)$$

where the elastic moduli C_{11} and C_{12} are 165.77 and 63.93 GPa, respectively.[4] Thus, we can use the measured values of $a_{\|}$ for the evaluation of either x or N_B, provided the remaining value is known. Consequently, for $N_B = 1.33 \times 10^{20}\,cm^{-3}$, we find the Ge content of our samples proportional to the germane flow with the coefficient of 0.0218 slm^{-1}. The in-plane strain values in the layers are 0.069% (no Ge), 0.0604% (0.2 slm), 0.043% (0.4 slm), 0.027% (0.6 slm), 0.018% (0.7 slm), 0.013% (0.8 slm), −0.006% (1.0 slm), and −0.018% (1.2 slm, from the smaller value of the perpendicular lattice constant). The strain compensation has been achieved at $x = 0.019$ (9.5×10^{20} Ge atoms in cm^3); this corresponds to 7.1 Ge atoms per one B atom, slightly more than 6.5 found in Ref. 1.

Contrary to the X-ray data, optical spectra are sensitive to the individual content of B and Ge. Namely, the infrared response is dominated by the free-hole plasma, generated by the electrically active boron impurities, with almost negligible influence of the Ge concentration. The characteristic Drude-like response is apparent in the ellipsometric data of Fig. 2, together with the Fano-type resonance of the silicon lattice mode (at $\sim 520\,cm^{-1}$) with the continuum of direct intervalence electronic transitions.[5,6] The plasma resonance is best seen in the negative inverse of the dielectric function (inset of Fig. 2); its spectral position and width is directly related to the free carrier density and relaxation rate, respectively. Both of these values are essentially independent of x, which confirms the same free hole density and shows a negligible contribution of Ge atoms to the scattering rate (the latter is mainly due to the boron ions). The Drude fits of the spectra at low frequencies ($\leq 500\,cm^{-1}$) lead to the free-hole density of $1.33 \times 10^{20}\,cm^{-3}$, in a good agreement with the target value of $1.5 \times 10^{20}\,cm^{-3}$.

We have also collected reflectance spectra in MIR; owing to the low level of noise, we were able to suppress the flat Drude-like background and enhance weaker and sharper structures, by numerical differentiation. Shown in Fig. 3 are the derivatives plotted on expanded scales at smaller wavenumbers. The Fano resonance of the silicon transverse and longitudinal optical mode is very pronounced, changing little with added Ge. In addition, composite structures appear in the range of from 600 to 660 wavenumbers. We assign them to localized boron vibrations, enhanced by the Fano-like coupling with the intervalence electronic transitions (note the similarity of the 520 and $620\,cm^{-1}$ lineshapes). This assignment is supported by the isotopic composition of natural boron, 80% of ^{11}B and 20% of ^{10}B, and the spectral position of the localized vibrations detected in absorption measurements.[7] After a detailed analysis and understanding of the spectral features due to the lattice vibrations, they are likely to provide a convenient metrological tool for the heavy boron doping. The penetration depth of light in the samples with the free-hole concentration of $1.3 \times 10^{20}\,cm^{-3}$ is about 400 nm at $600\,cm^{-1}$, almost independent of the Ge content. Thus, only a fraction of the 3.5 μm epilayers is probed. On the other hand, the material becomes transparent above $\sim 4000\,cm^{-1}$; we have detected small Fabry-Perot oscillations in the reflectance and ellipsometric spectra, resulting from the (weak) optical contrast between the SiGe:B layers and Si substrate in this spectral range. Their period is in a

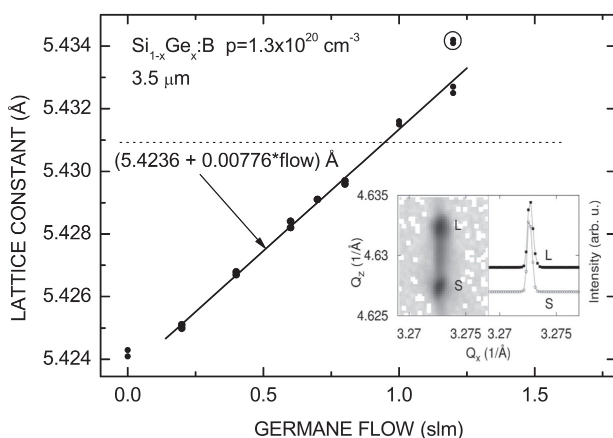

FIG. 1. In-plane (dotted line) and out-of-plane (symbols; solid line: the best linear fit) lattice constants of strained SiGe:B epilayers. The circled outliers for the 1.2 slm sample indicate an inhomogeneity of this sample in the growth direction. Inset: asymmetric 224 reciprocal space map for the 0.2 slm sample (left part); line scans through the substrate (S) and epilayer (L) peaks (right part).

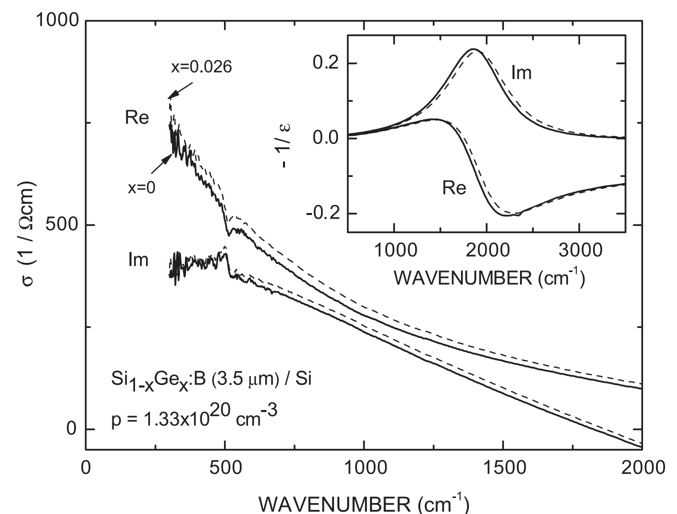

FIG. 2. Complex conductivity measured ellipsometrically on the sample with zero (solid lines) and maximum ($x = 0.026$, dotted lines) Ge content. Inset: negative inverse of the dielectric function in the range of plasma resonance.

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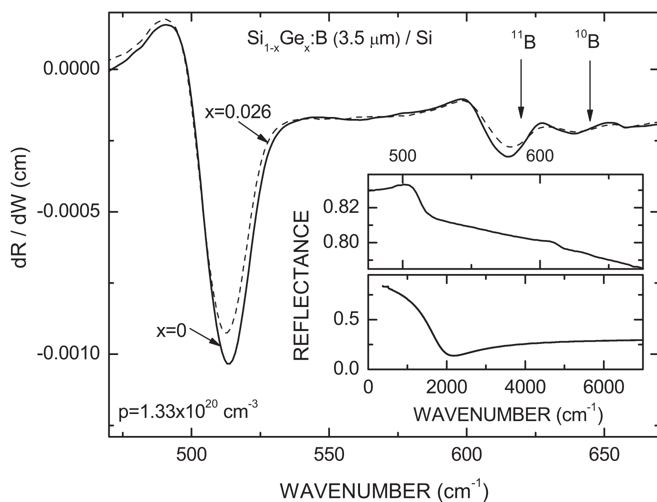

FIG. 3. Numerically differentiated reflectance of the samples with zero (solid lines) and maximum (dotted lines) Ge content. The vertical arrows point to the positions of the localized vibration of the two boron isotopes. Inset: reflectance spectrum in the whole measured range (lower part) and on expanded scales (upper part).

fair agreement with the average value of 3.5 μm of the epilayer thickness.

The results obtained from spectroellipsometric measurements in the visible and ultraviolet range are summarized in Fig. 4. Interband electronic transitions E_1, influenced by the boron doping and strain in the epilayers, clearly shift to lower photon energies with increasing Ge content. We have enhanced the spectral structures by numerical differentiation and used the procedure of extracting the E_1 gap energy from symmetrized linear combinations of the real and imaginary parts of the derivatives.[8] For parabolic joint density of states, the retrieved energy is independent of the order of derivative, the type of the critical point, its broadening energy, and the phase factor describing excitonic effects.[8] We have minimized the asymmetric part of the linear combination in the range from 3.03 to 3.63 eV, obtaining the energies shown in Fig. 4. Since the flow of 1 slm corresponds to the Ge content x of 0.0217, we arrive at the linear dependence $E_1 = (3.335 - 1.01\,x)$ eV. Its slope is smaller than that found recently for thin strained layers of undoped SiGe with $x \leq 0.75$, $E_1 = (3.373 - 1.22\,x)$ eV, resulting from the linear fit of data from Table II of Ref. 9. The difference might be caused by the heavy boron doping of our samples. Note that the dependence is even steeper for relaxed SiGe, $E_1 = (3.395 - 1.44\,x)$ eV, resulting from the quadratic dependence for small x.[10] The ellipsometric measurements lead to the penetration depth of light of about 100 nm at the center of E_1 spectral structure. Consequently, the probed volume is much smaller than that of X-ray measurements, where the whole thickness of the epilayer contributes to the measured signals.

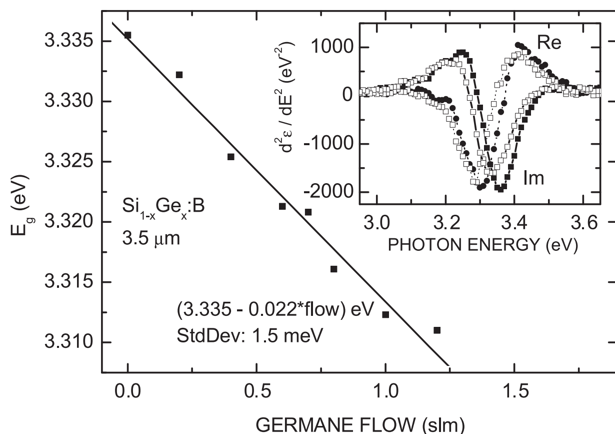

FIG. 4. The energy of E_1 transitions (full symbols) obtained from the symmetrized 2nd derivative lineshapes for all studied samples; the best linear fit (solid line). Inset: real (dotted lines) and imaginary (solid lines) of the second derivatives calculated numerically from the (pseudo)dielectric functions of the zero (full symbols) and maximum (germane flow of 1.2 slm, $x = 0.026$; empty symbols) Ge content.

The presence of B and Ge in the Si lattice can also be detected using the very simple reflectance technique in the range of E_1 transitions. We show in Fig. 5 the ratio of reflected intensity of the measured and reference sample, the latter being that of zero Ge content. The bottom spectrum has been taken after the remaining samples in the whole series; it indicates the noise and drift levels in the measurements. As the interband transitions shift to lower energies with increasing x, the characteristic s-like shape develops in the relative reflectance with the extent exceeding 0.02 for the largest Ge content. Since the noise level of the relative reflectance at individual spectral points is about 0.001, and about 150 points enter the subsequent analysis, fairly precise values of the magnitude of this effect are available. We have fitted the j-th measured lineshape $R_j(E)$, in a suitable window of the photon energies E, by $F_j R_{j0}(E) + S_j$, where $R_{j0}(E)$ is a selected spectrum from the series. The constant S_j accounts for usual (typically $\leq$0.005) rigid shifts of the spectra caused by the irreproducibilities of mounting the samples. We have selected the data for the 0.8 slm flow as the reference and assigned it the value of $x = 0.0174$ obtained from the X-ray measurements. Assuming a linear scaling of F_j with the Ge content, we arrived at the results shown in the right panel of Fig. 5.

The reflectance data are collected quickly, from a fairly small spot, and can be utilized for mapping the in-plane homogeneity of the wafers. In fact, we did not find deviations of the Ge content above the detection limit of ~0.001 in

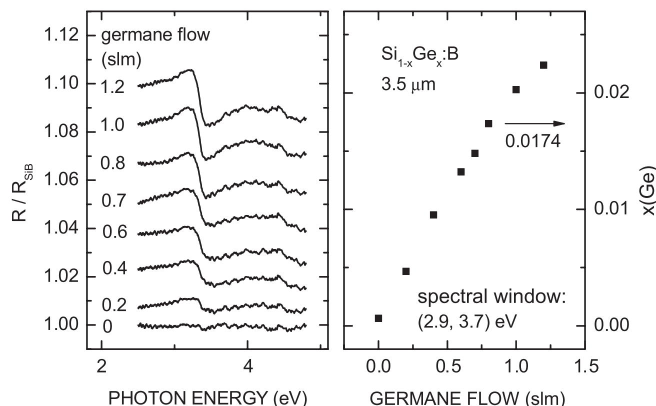

FIG. 5. Left panel: reflectance spectra measured relatively to the boron-doped silicon (zero germane flow). The spectra are shifted vertically for clarity. Right panel: the Ge content derived from the magnitude of the spectral structure in the window centered at 3.3 eV; the horizontal arrow indicates the Ge content assigned to the 0.8 slm sample.

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scanning the surfaces of our samples. Standard deviation of individual values of x shown in Fig. 5 from the best-fit linear dependence on the germane flow is 0.0009. Thus, the noise in the values of Ge content is about a factor 1.5 smaller than that of ellipsometry. Similar to the ellipsometric measurements, only a fraction of the epilayer close to the surface is probed using this technique; this is probably the reason why we have not seen the peculiar behavior of the 1.2 slm sample shown Fig. 1.

In conclusion, we have grown a series of thick pseudomorph $Si_{1-x}Ge_x$ layers, $x \leq 0.026$. The X-ray studies reveal that the strain due to the boron doping of $1.33 \times 10^{20}\,cm^{-3}$ is compensated by Ge at $x = 0.0204$, i.e., the Ge concentration of $10.2 \times 10^{20}\,cm^{-3}$. Infrared spectra are sensitive to the boron concentration; we have observed spectral structures related to the localized vibrations of boron ions in differentiated reflectance. Fingerprints of the variations of Ge content are clearly present in the optical spectra around the E_1 transitions. In particular, the simple relative reflectance spectroscopy using multichannel spectrometers has been found to be fairly sensitive and suitable for assessing the wafer homogeneity.

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