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Strain relaxation in thin $Si_{1-x-y}Ge_xC_y$ layers on Si substrates

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The possibility to obtain a heterosystem consisting of the upper partially strained and lower relaxed layers by gradient *in situ* doping of SiGe layers with carbon is considered. The properties of the as-grown and annealed (600 to 1000°C) samples have been studied by Raman spectroscopy and atomic force microscopy. The strain relaxation degree in the as-grown layers as estimated from the Raman spectra amounts 50 % for $Si_{0.7-y}Ge_{0.3}C_y$ and 0 % for $Si_{0.9-y}Ge_{0.1}C_y$. During the annealing, the strain has been found to be relaxed not homogeneously over the whole structure but in a layer-by-layer way. The segregation of carbon atoms is observed for both types of as-grown $Si_{1-x-y}Ge_xC_y$ layers in the near-substrate regions.

Рассмотрена возможность получения отрелаксированных SiGe слоев на кремниевой подложке, градиентно *in situ* легированных углеродом в процессе эпитаксии. Используя спектроскопию комбинационного рассеяния света (КРС) и атомную силовую микроскопию, исследованы свойства исходных образцов и образцов после термических обработок в диапазоне температур 600–1000°C. Из спектров КРС оценена степень пластической релаксации в исходном $Si_{0,7-y}Ge_{0,3}C_y$ (50 %) и $Si_{0,9-y}Ge_{0,1}C_y$ (0 %) слоях. Установлено, что релаксация напряжений при отжигах происходит не однородно по всему объему, а послойно. В обоих типах $Si_{1-x-y}Ge_xC_y$ слоев происходит сегрегация углерода на интерфейсах с Si подложками.

Modern semiconductor electronics is based predominantly on silicon technology. The use of SiGe alloys is one of the most efficient and promising ways to expansion and improvement of the parameters of Si-based electronic devices [1–3]. The SiGe-on-Si technology is developed in three main directions, aimed at formation of (i) fully relaxed buffer layers [4], (ii) fully strained layers for active IC elements [5], and (iii) self-assembled quasi-zero-dimensional nanoislands for application in both nano- and optoelectronics [6, 7]. The strain-free (relaxed) $Si_{1-x}Ge_x$ buffer layers (buffers) are used widely for subsequent growing of thin coherent Si layers with band structure modified by tensile strains existing therein [8]. Thus, electrical and optical properties of such active Si layers can be tuned easily by varying the strain value which is defined by the lattice mismatch with the underlying buffer, i.e. by the buffer chemical composition x and/or its strain relaxation degree.

For application in devices, the $Si_{1-x}Ge_x$ buffer should satisfy several conditions. First, it should be relaxed. Second, its surface roughness should be low enough to avoid the quality deterioration of the upper active Si layer. Third, to provide high-quality device structures, the surface density of threading dislocations (TDs) should be as low as possible, not exceeding 10^5 – 10^6 cm^{-2} [3]. The buffer layers are usually $Si_{1-x}Ge_x$ alloys with Ge content increasing from bottom to top, so-called gradient layers [2]. The lattice constant on the surface of such

a fully relaxed buffer depends only on the x value, and the threading dislocation density is minimized by a very smooth gradient of Ge content (about 10 % Ge/μm). Due to the very small variation of strain within the layer, caused by the smooth Ge gradient, the misfit dislocation (MD) nucleation rate is lowered. As a result, the MDs are distributed over the whole layer thickness, reducing the probability of blocking of movable TDs. Moreover, during the growth, the most strained top layer creates forces stimulating of the TD sliding out of the layer. One of the disadvantages of the graded SiGe buffers is their inevitably large thickness (1–10 μm), caused by the small Ge gradient, and resulting in high surface roughness.

In this work, the possibility to obtain thin SiGe buffers by *in situ* stepwise doping with carbon is considered. The covalent radius of carbon atom is known to be much smaller (0.77 Å) than those of Si (1.1 Å) and Ge (1.22 Å). Thus, replacement of Si or Ge atoms in SiGe layer by carbon results in a reduction of the average lattice constant. Both simulations and experiments show that 1 % of substitutive carbon atoms compensates 10 % to 12 % of Ge [1, 9]. Therefore, the desirable value of $Si_{1-x-y}Ge_xC_y$ layer lattice constant can be achieved by the appropriate choice of the carbon concentration y. This work was aimed at the investigation of samples grown with the stepwise decrease of y value in the course of growing at constant x instead of usually employed increase of x. An identical variation of carbon content y from 1.5 to 0.4 % was performed for two concentrations of Ge (10 and 30 %).

The samples under investigation were 70 nm thick $Si_{0.7}Ge_{0.3}$ and $Si_{0.9}Ge_{0.1}$ layers grown on Si(100) substrates by chemical vapor deposition. In the course of growth, the layers were doped with carbon in a step-by-step manner, resulting in four sublayers, each about 17 nm thick, with carbon content of 1.5 %, 1.2 %, 0.8 % and 0.4 %, respectively (Fig. 1, a). Some samples were annealed during 10 min at 600 to 1000°C in N_2 atmosphere. The structures were studied by Raman scattering spectroscopy and atomic force microscopy (AFM). The Raman spectra were taken using a double-grating LOMO DFS-24 spectrometer at room temperature. The 487.9 nm Ar^+ laser line was used to excite the spectra. The signal was registered with a cooled FEU-136 photomultiplier operated in the photon counting mode. The known frequencies of the Ar^+ laser discharge lines were used to measure exactly the Raman band frequencies. The surface morphology of the SiGe layers was studied using Digital Instruments NanoScope IIIa atomic force microscope operated in the tapping mode.

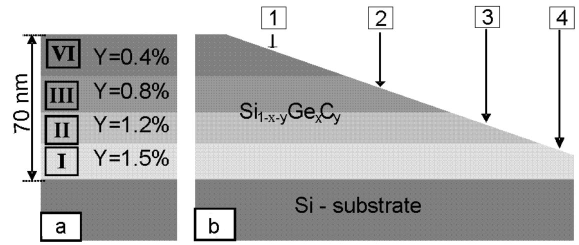

Fig. 1. Scheme of the as-grown $Si_{0.7-y}Ge_{0.3}C_y$ sample (a) and the wedge-like sample prepared by ion sputtering for the measurements of strain distribution over the layer thickness (b).

The AFM image of the $Si_{0.7-y}Ge_{0.3}C_y$ layer surface is shown in Fig. 2a. The layer surface is of high quality, as the roughness does not exceed 1 nm (Fig. 2b). Furthermore, the absence of so called "cross-hatched" structure is an evidence for low TD density. The AFM studies of the $Si_{0.9-y}Ge_{0.1}C_y$ surface revealed even lower surface roughness.

Fig. 3 shows Raman spectra of $Si_{0.7-y}Ge_{0.3}C_y$ (curve *1*) and $Si_{0.9-y}Ge_{0.1}C_y$ (curve *2*) layers. In both spectra, a lower-frequency band attributed to Si–Si vibrations in the $Si_{1-x-y}Ge_xC_y$ alloy layer is observed along with a band at 520.0 cm^{-1} due to the scattering on the substrate LO phonons. The dependence of the Si–Si mode frequency for $Si_{1-x}Ge_x$ layers on Si on the composition x and strain is well known [10, 11]:

$$\omega = \omega_0 - 68 \cdot x - 815 \cdot \varepsilon(x), \qquad (1)$$

where ω_0 is the LO phonon frequency in bulk silicon (520.0 cm^{-1}); $\varepsilon(x)$, the elastic strain in the $Si_{1-x}Ge_x$ layer, equal to its lattice mismatch to the Si substrate:

$$\varepsilon(x) = \frac{a_{Si} - a_{SiGe}}{a_{Si}} \qquad (2)$$

where a_{Si} and a_{SiGe} are the lattice parameters of Si and $Si_{1-x}Ge_x$ layer, respectively.

To describe the Si–Si mode dependence for $Si_{1-x-y}Ge_xC_y$ layer, the following empirical expression was used in [12]:

$$\omega = \omega_0 - 68 \cdot x - 830 \cdot \varepsilon(x,y), \qquad (3)$$

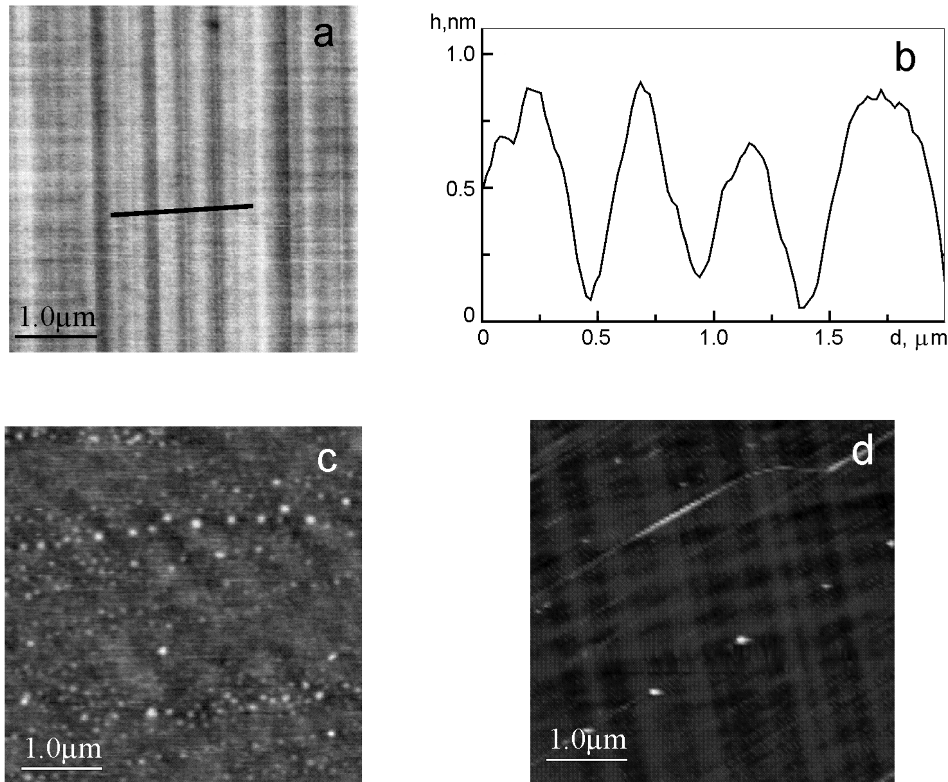

Fig. 2. AFM image of the $Si_{0.7-y}Ge_{0.3}C_y$ layer surface (a) and corresponding surface roughness profile (b). AFM images of the $Si_{0.9-y}Ge_{0.1}C_y$ (c) and $Si_{0.7-y}Ge_{0.3}C_y$ (d) surfaces in craters near the substrate.

where

$$\varepsilon(x,y) = \frac{a_{Si} - a_{SiGeC}}{a_{Si}}. \quad (4)$$

However, the experimental ω_{Si-Si} values for fully strained $Si_{1-x-y}Ge_xC_y$ layers with different y lie above the theoretical line (3) [12]. This discrepancy can be due to two reasons: the lattice distortion caused by a significant difference in bond lengths of Si–Si, Ge–Si, and C–Si, resulting in the reduction of the Si–Si bond length and/or additional compression of the lattice by interstitial carbon atoms. An empirical equation derived in [13] is a better fit to the experimental data than Eq.(3):

$$\omega = \omega_0 - 68 \cdot x + 190 \cdot y - 830 \cdot \varepsilon(x,y). \quad (5)$$

In this work, we use Eq.(5) to determine the strain values in our $Si_{1-x-y}Ge_xC_y$ layers. From the experimental Raman spectra of the $Si_{0.7-y}Ge_{0.3}C_y$ structure, we derived $\omega_{Si-Si} = 505.2$ cm^{-1} (Fig. 3, curve *1*). In order to analyze the strain value in the layer basing on the experimental data, we calculated ω_{Si-Si} for the two limiting

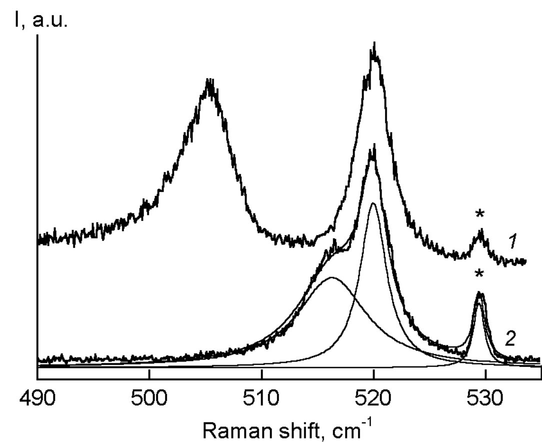

Fig. 3. Raman spectra of the as-grown $Si_{0.7-y}Ge_{0.3}C_y$/Si (*1*) and $Si_{0.9-y}Ge_{0.1}C_y$/Si (2) layers. The asterisks denote the Ar^+ plasma lines.

cases: fully relaxed and fully strained $Si_{0.7-y}Ge_{0.3}C_y$ layer.

In the first case ($\varepsilon(x, y) = 0$, $y = 0.015$), according to Eq.(5), $\omega_{Si-Si} = 502.5$ cm^{-1}. In the second case, the substitutive carbon content was supposed to be 1.5 % at the $Si_{1-x-y}Ge_xC_y$/Si interface and 1.2 %, 0.8 %,

Table. Lattice constants of Si, Ge and diamond, and misfit parameters for all sublayers.

Sample	Diamond	Ge	Si	Si substrate	$Si_{1-x-y}Ge_xC_y$ (x=0.3)			
					I_{SiGe}	II_{SiGe}	III_{SiGe}	IV_{SiGe}
					$y = 1.5$	$y = 1.2$	$y = 0.8$	$y = 0.4$
Lattice constant	3.567	5.657	5.431		5.471	5.477	5.484	5.491
Misfit parameter, f					0.0073	0.0009	0.0015	0.0013

and 0.4 % in the three upper sublayers. The average lattice parameter values for sublayers with different carbon concentration were determined according to Vegard law:

$$a_{SiGeC} = (1 - x - y) \cdot a_{Si} + x \cdot a_{Ge} + y \cdot a_C. \quad (6)$$

In Eq.(6), a_C was assumed to be equal to diamond lattice parameter, which is the best fit of the Vegard law to the real situation [9]. The strain values that equal to the lattice misfit at the absence of plastic relaxation were determined from Eq.(4) for each of the four sublayers (Fig. 1a) and are listed in Table. For the fully strained interfacial sublayer with $y = 1.5$ %, according to Eq.(5), $\omega_{Si-Si} = 508.1$ cm^{-1}. The experimental value 505.2 cm^{-1} is much smaller and reveals a significant plastic relaxation of the layer. The plastic relaxation degree δ for the $Si_{1-x-y}Ge_xC_y$ sublayers was quantitatively estimated as [14]

$$\delta = \frac{\varepsilon_{xy} - \varepsilon_{exper}}{\varepsilon_{xy}}, \quad (7)$$

where ε_{xy} is the (calculated) strain in the $Si_{1-x-y}Ge_xC_y$ sublayer due to its misfit to the substrate (Table); ε_{exper}, the strain derived from the experimental ω_{Si-Si} values in the Raman spectrum by solving equation $520.0-68\cdot0.3+190\cdot y-830\cdot\varepsilon_{exper} = 505.2$ (cm^{-1}). By substituting ε_{xy} and ε_{exper} for $Si_{0.685}Ge_{0.3}C_{0.015}$ into Eq.(7), we obtained the value of $\delta = 0.50$. Therefore, the *in situ* doping of $Si_{0.7}Ge_{0.3}$ layer with the indicated carbon concentration reduces the layer lattice misfit to the substrate, but simultaneously a significant (50 %) plastic relaxation occurs. The real δ value can be even higher because not all carbon atoms are incorporated substitutionally and contribute to relaxation, as was supposed in calculations.

It should be noted that the experimental Raman band (Fig. 3, curve *1*) is asymmetric having a full width at half maximum

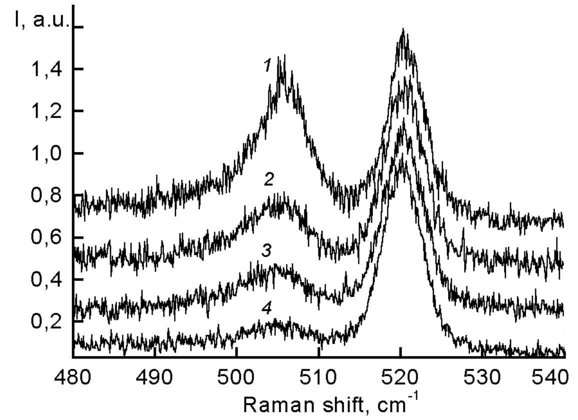

Fig. 4. Raman spectra taken from the points *1*, *2*, *3*, *4* on the $Si_{0.7-y}Ge_{0.3}C_y$ wedge-like structure of Fig. 1.

(FWHM) of about 2 times larger than that of the Si substrate. Such a band shape can be caused by contributions from the sublayers with different δ and/or high density of structural defects. To map the strain distribution over the whole $Si_{1-x-y}Ge_xC_y$ layer, a wedge-like sample was prepared by ion sputtering (Fig. 1b). The relative intensity of the epilayer-related Raman peak decreases, when going from point 1 to point 4 on the wedge-like sample, and the ω_{Si-Si} shifts slightly to lower frequencies (Fig. 4, curves *1–4*). The FWHM of the Raman peak is the same for all sublayers what is an evidence of the observed peak broadening to be caused by structural defects and significant local strains. Indeed, it was shown in [1, 15] that, despite the macroscopic strain in $Si_{1-x-y}Ge_xC_y$ layer can be completely eliminated by an appropriate choice of carbon concentration, a high local strain around the carbon atoms remains.

For the sample with the lower Ge content ($Si_{0.9-y}Ge_{0.1}C_y$), the calculated value of $\omega_{Si-Si} = 516.5$ cm^{-1} almost coincides with the experimental value of 516.3 cm^{-1} (Fig. 3, curve *2*). Thus, no plastic relaxation occurs in this case because of the subcritical layer thickness for the given x [16], and the pres-

ence of carbon atoms further reduces the mismatch. This conclusion was additionally confirmed by AFM measurements. The craters penetrating the whole $Si_{0.9-y}Ge_{0.1}C_y$ layer were made by ion sputtering. The AFM images from the near-interface regions of the structure reveal the absence of cross-hatches, while chains of islands (Fig. 2c) were observed being most likely carbon precipitates. For $Si_{0.7-y}Ge_{0.3}C_y$ layer, the density of the islands was much lower, although their size was larger (Fig. 1d). Moreover, the cross-hatch network (Fig. 2d) evidencing a high MD density in the $Si_{0.7-y}Ge_{0.3}C_y$ structure.

One of the most important features of $Si_{1-x-y}Ge_xC_y$ is its thermal stability. The temperature effect on the layer structure was studied by annealing the samples at temperatures from 600 to 1000°C during 10 min in N_2 atmosphere. The Raman spectra of the as-grown and annealed samples with $x = 0.3$ are shown in Fig. 5. The temperature-induced strain relaxation is seen to start at 800°C (curve *3*), manifesting itself in the low-frequency shift and broadening of the Raman band. For the sample annealed at 900°C (curve *4*), the Si–Si band appears as a superposition of two peaks at 499 and 504 cm^{-1}. The lower-frequency maximum corresponds to the fully relaxed $Si_{0.7}Ge_{0.3}C_y$ alloy and is obviously related to the near-interface layer with $y = 0.015$ and the next one with $y = 0.012$. Two upper layers remain partially strained and cause the peak at 504 cm^{-1}. We explain the observed doublet structure of the Si–Si Raman band as follows. As the largest lattice mismatch takes place between the (interfacial) sublayer I and the substrate and between the sublayers II and III (Table), the annealing at temperatures not exceeding 800°C initiates MDs mainly at the SiGeC/Si interface, and this helps the strain relaxation of the SiGeC layer as a whole. Annealing at 900°C leads to a substantial increase of the MD density at the interface between the sublayers II and III. As a result, the sublayers I and II relax completely while III and IV ones remain partially strained what is revealed in the structure of the Raman band (Fig. 5, curve *4*). As a limiting case of such a kind of stepwise doping, a structure with only two sublayers differing in carbon content can be obtained, with upper layer being partially strained and the lower one (with a higher C content) completely relaxed. The frequency position of the Si–Si band for the samples annealed at 1000°C (Fig. 5, curve *5*)

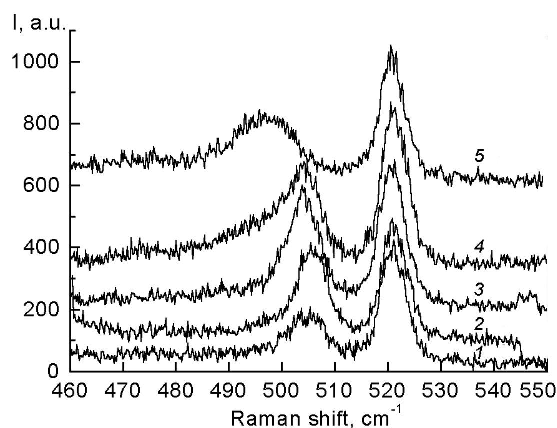

Fig. 5. Raman spectra of the as-grown $Si_{0.7-y}Ge_{0.3}C_y$ layer (*1*) and annealed during 10 min in ambient N_2 at 700°C (2); 800°C (*3*); 900°C (*4*); 1000°C (*5*).

reveals the full relaxation of the whole $Si_{1-x-y}Ge_xC_y$ layer.

In conclusions, the possibility to obtain a heterosystem consisting of the upper partially strained and the lower relaxed sublayers by stepwise *in situ* doping of SiGe layers by carbon was demonstrated. The surface quality of the as-grown structures is very high, with the surface roughness not exceeding 1 nm. The strain relaxation degree in the as-grown layers was estimated from the Raman spectra as 50 % for $Si_{0.7-y}Ge_{0.3}C_y$ and zero for $Si_{0.9-y}Ge_{0.1}C_y$. The $Si_{0.7-y}Ge_{0.3}C_y$ layer was shown to be stable to annealing up to 700°C. Moreover, the strain relaxes during annealing not homogenously over the whole structure but in a layer-by-layer way. The segregation of carbon atoms is observed for both types of as-grown $Si_{1-x-y}Ge_xC_y$ layers in the near-substrate regions.

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Релаксація напружень у тонких шарах $Si_{1-x-y}Ge_xC_y$, сформованих на кремнієвих підкладках

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Розглянуто можливість отримання відрелаксованих SiGe шарів на кремнієвій підкладці, що градієнтно *in situ* легувалися вуглецем у процесі епітаксії. Використовуючи спектроскопію комбінаційного розсіювання світла (КРС) та атомну силову мікроскопію, досліджено властивості вихідних зразків та зразків після термічних обробок у діапазоні температур 600–1000°C. Із спектрів КРС оцінено ступінь пластичної релаксації у вихідному $Si_{0,7-y}Ge_{0,3}C_y$ (50 %) та $Si_{0,9-y}Ge_{0,1}C_y$ (0 %) шарах. Встановлено, що при відпалах релаксація напружень відбувається не однаково по всьому об'єму, а пошарово. В обох типах $Si_{1-x-y}Ge_xC_y$ шарів на їх інтерфейсах з Si підкладками відбувається сегрегація вуглецю.