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Germanium content and strain in $Si_{1-x}Ge_x$ alloys characterized by Raman spectroscopy

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ABSTRACT

Previous Raman spectroscopy studies on SiGe alloys have left rather large uncertainties concerning the relationships between the Raman peaks' frequency shifts and stress. In this paper, we systematically revisit these relationships, confirm some coefficient values and propose new relationships linking the Raman peak shift to stress and Ge concentration. Different types of stacks were grown and studied to that end:

(1) Thick, nearly fully relaxed SiGe virtual substrates grown on Si (001), whose lattice parameter is close to that of bulk material for a given Ge composition (in-between 20% and 100%).

(2) Thin, fully compressively-strained SiGe layers grown on Si (001), with a Ge content in the 5–55% range.

The cross-examination with Raman spectroscopy and X-ray diffraction of those stacks provided us with precise values of the coefficients linking the Raman peak shift to (i) the Ge content of the SiGe layer (thanks to SiGe virtual substrates) and (ii) the magnitude of stress in the SiGe layer (thanks to thin, fully pseudomorphic layers).

1. Introduction

SiGe virtual substrates are widely used as templates for the fabrication of high electron mobility strained Silicon-On-Insulator (s-SOI) substrates [1]. Given that tensile strain in the sSi layer on top is controlled by the virtual substrate lattice parameter, it is necessary to accurately control the strain and the composition in it. Raman spectroscopy can be used to extract both [2]. This non-destructive measurement technique can also be used to monitor Ge content and strain in thin, compressively strained SiGe layers used as high hole mobility channels in advanced p-type Metal Oxide Semiconductor Field Effect Transistors [3,4].

In the present study, we have accurately quantified the evolution of the Raman spectra of $Si_{1-x}Ge_x$ layers over the full range of Ge concentrations (i.e. 0–100%). We have notably extracted the Raman peak shifts as a function of the Ge content and strain in (i) thick, nearly fully relaxed SiGe layers and (ii) thin, compressively-strained layers thanks to a large number of dedicated samples spanning a much wider Ge concentration range than in previous studies (20–100% for thick layers, 0–55% for thin layers).

2. Experimental protocol

Two types of layers or stacks were grown on 200mm Si wafers in an Epi Centura 5200 Reduced Pressure – Chemical Vapor reactor for this study. The first batch consisted in thick $Si_{1-x}Ge_x$ virtual substrates grown at high temperatures (850–900 °C) on Si(001). Thanks to the confinement of most of the misfit dislocations in the linearly graded SiGe layers underneath (grading: ~8–10% Ge/μm), the roughly one micron thick, constant composition SiGe layers sitting on top of our virtual substrates were almost fully relaxed (Ge content between 20% and 100%) [5,6]. Several tens of nm thick, fully compressively-strained $Si_{1-x}Ge_x$ layers ($0.05 \le x \le 0.55$) were otherwise grown on Si(001). Growth temperature (between 750 °C and 550 °C) and thickness were carefully chosen in order to definitely stay below the critical thickness for plastic relaxation of SiGe on Si [7].

The Ge concentration and, in SiGe virtual substrates, the macroscopic degree of strain relaxation *R*, were determined from high resolution X-ray diffraction experiments performed on a Panalytical X'Pert Pro tool. Raman measurements on thick, nearly fully relaxed SiGe virtual substrates gave us access to, A^{Si-Si}, A^{Si-Ge} and A^{Ge-Ge}, the coefficients linking the shift of the Si–Si, Si–Ge and Ge–Ge vibrations to the germanium concentration as defined in Eq. (1) just below. Knowing those parameters, measurements on thin, fully compressively strained SiGe layers can be used to extract b^{Si-Si}, b^{Si-Ge} and b^{Ge-Ge}, the coefficients giving the shift of

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the Si–Si, Si–Ge and Ge–Ge peaks as a function of the in-plane strain (Eq. (1)). In the germanium concentration range for which the following bilinear relations are valid (i.e. where Raman peak are actually observed), the frequencies of the Si–Si, Si–Ge and Ge–Ge peaks are indeed given by

$$\omega^{\mathrm{Si-Si}} = \omega_0^{\mathrm{Si-Si}} - A^{\mathrm{Si-Si}}x + b^{\mathrm{Si-Si}}\varepsilon_{//}$$
$$\omega^{\mathrm{Si-Ge}} = \omega_{0,x\to 0}^{\mathrm{Si-Ge}} - A^{\mathrm{Si-Ge}}x + b^{\mathrm{Si-Ge}}\varepsilon_{//}$$
$$\omega^{\mathrm{Ge-Ge}} = \omega_0^{\mathrm{Ge-Ge}} - A^{\mathrm{Ge-Ge}}x + b^{\mathrm{Ge-Ge}}\varepsilon_{//} \qquad (1)$$

Here $\omega^{\mathrm{X-Y}}$ (where X, Y stand for Si or Ge) are the experimental wavenumbers, $\omega_0^{\mathrm{X-Y}}$ are the T_{2g} silicon and germanium peak frequencies, x is the germanium content and $\varepsilon_{//}$ is the in-plane strain for growth along the (001) direction. $\omega_{0,x\to 0}^{\mathrm{Si-Ge}}$ is the frequency of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ for x close to 0. Raman spectra were recorded in the backscattering geometry using a Jobin Yvon T64000 triple monochromator equipped with a liquid N_2 cooled charge coupled device detector. The light was focused onto the sample surface thanks to a 100 × (0.9 numerical aperture) short working objective. The resulting spot diameters were around 0.8 μm. The excitation wavelength λ was 514 nm from an Ar^+ laser with a typical laser power of ~1 mW. The optical penetration depth of the light into $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ depends on the composition of the alloy and the wavelength. At $\lambda = 514$ nm, it decreases from 760 nm (for pure Si) down to 19 nm only (for pure Ge). A reference spectrum was systematically acquired on bulk Si (001) in order to avoid any spectrometer calibration problem. For the majority of the samples the data were collected on 20 different locations on the samples. No significant variations were observed, with values lying within the experimental error limits. The spectral lines used for the analysis were fitted with Lorentzian functions in order to increase accuracy. For each sample considered, the peak frequencies were extracted from an average spectrum obtained by adding 20 individual spectra randomly recorded on the sample surface. The deleterious impact of periodic strain fluctuations in our SiGe virtual substrates (which give birth to the surface cross-hatch typical of such stacks) was thus minimized.

3. Results

In a typical Stokes Raman spectrum of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys, three well defined peaks are observed at about 500, 400 and 300 cm^{-1}. They correspond to the so-called Si–Si, Si–Ge and Ge–Ge modes, respectively [8–10]. Low intensity peaks at 420 and 480 cm^{-1} are coming from peculiar $\mathrm{Si–Si}_{local}$ vibrational modes due to fluctuations of the number of Ge atoms in the vicinity of Si ones. The frequencies of the main optical modes are functions of the germanium content, as illustrated in Fig. 1.

Frequency variations are the results of (i) bond length variations in SiGe alloys (compared to bond lengths in pure silicon and pure germanium) and (ii) structural "*disorder*" induced by the random arrangement of silicon and germanium atoms. Because of bond length variations, the frequency of the Si–Si mode decreases and the frequency of the Ge–Ge mode increases as the Ge content in SiGe alloys increases. Meanwhile, the mass disorder effect will lead to an asymmetrical broadening and to a downshift of both modes. The convolution of both effects explains the evolution of the Raman peaks with Ge concentration shown in Fig. 2 for SiGe virtual substrates. The curve linking the SiGe mode frequency shift to the Ge content has notably a bell-like shape, with a maximum close to 50% [11–14]. The precise determination of Raman shifts allowed a more reliable evaluation of $A^{\mathrm{X-Y}}$ and $b^{\mathrm{X-Y}}$ coefficients over a larger Ge concentration range and with far more data points than previously investigated/reported so far. We ended up with the following relationships:

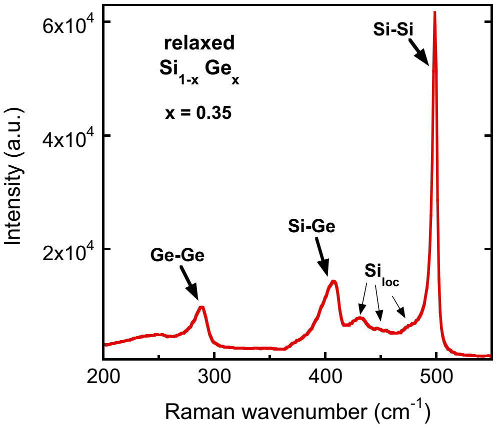

Fig. 1. Raman spectrum associated with a SiGe 35% virtual substrate grown on Si(001). Three main modes are present, i.e. Si–Si ($\omega^{\mathrm{Si-Si}} = 500\ \mathrm{cm}^{-1}$) Si–Ge ($\omega^{\mathrm{Si-Ge}} = 402\ \mathrm{cm}^{-1}$) and Ge–Ge ($\omega^{\mathrm{Ge-Ge}} = 287\ \mathrm{cm}^{-1}$).

$$\omega^{\mathrm{Si-Si}} = \omega_0^{\mathrm{Si-Si}} - 62x - 850\varepsilon_{//} \quad x \le 0.6$$
$$\omega^{\mathrm{Si-Ge}} = \omega_{0,x\to 0}^{\mathrm{Si-Ge}} + 24.3x - 551\varepsilon_{//} \quad 0.3 \le x \le 0.5$$
$$\omega^{\mathrm{Ge-Ge}} = \omega_0^{\mathrm{Ge-Ge}} + 6.9x - 403\varepsilon_{//} \quad 0.3 \le x \le 0.55 \qquad (2)$$

We will now describe how those results were found.

3.1. *Determination of A^{Si-Si}, A^{Si-Ge} and A^{Ge-Ge} using SiGe virtual substrates*

We have used the Raman spectra associated with SiGe virtual substrates to accurately determine $A^{\mathrm{Si-Si}}$, $A^{\mathrm{Si-Ge}}$ and $A^{\mathrm{Ge-Ge}}$, the coefficients linking the shift of the Si–Si, Si–Ge and Ge–Ge vibrations to the germanium concentration. We had however to quantify possible influences of residual stresses on the values of those parameters.

Omega-2Theta scans around the (004) and the (224) XRD orders (grazing incidence and grazing exit) provided us with (i) the Ge content x in the constant composition SiGe layer sitting on top of our virtual substrate (thanks to [15]) from

$$a_{\mathrm{SiGe}} = 5.43105 + 0.2005x + 0.0263x^2 \qquad (3)$$

and (ii) the macroscopic degree of strain relaxation R of the said layer, defined as

$$R = \frac{a_{\mathrm{SiGe}}^{//} - a_{\mathrm{Si}}}{a_{\mathrm{SiGe}} - a_{\mathrm{Si}}}, \qquad (4)$$

where a_{SiGe} and $a_{\mathrm{SiGe}}^{//}$ are the lattice constants of bulk, unstrained SiGe and the in-plane lattice parameter of SiGe, respectively [16]. The increase of R with the Ge content x in our SiGe virtual substrates is shown in Fig. 3 (from 96.8% ($x = 0.2$) up to 103% ($x = 0.87$)). Such an evolution is most likely due to thermal expansion coefficients differences between SiGe and Si ($2.5 \times 10^{-6}\ \mathrm{K}^{-1}$ for silicon and $5.8 \times 10^{-6}\ \mathrm{K}^{-1}$ for germanium). The constant composition SiGe layer sitting on top of our virtual substrate, which is nearly fully relaxed at the growth temperature (850–900 °C), indeed sees its in-plane lattice parameter shrink with the thermal dilatation coefficient of Si substrate underneath, which is much thicker; meanwhile, its out-of-plane lattice parameter shrinks with that of SiGe. The increase of the SiGe thermal dilatation coefficient with the Ge content most likely explains the shift from slightly compressed to slightly tensily-strained layers seen in Fig. 3.

In the following, we will evaluate whether or not it is mandatory to take into account the small Raman shift caused by residual strain ε_r in SiGe virtual substrate in order to precisely