Acoustic Phonons in Periodical GeSiSn/Si Nanostructures

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Abstract. We apply Raman spectroscopy to study the phonon spectrum in periodical GeSiSn/Si nanostructures with Sn concentration varied from 0 to 20%. In the optical spectral region, an insignificant shift of the phonon mode positions with a variation of the Sn content prevents determination of Sn concentration relying only on the optical phonons behavior. In the acoustic region, we observe the doublets of the folded acoustic phonons, the spectral positions of which undergo the low-frequency shift with increasing the Sn content. The application of the elastic continuum model with the linear approximation of sound velocity via Sn content in GeSiSn layers fails to explain the experimental results. This indicates a nonlinear Sn concentration dependence of sound velocity in GeSiSn layers which describes well the positions of the folded acoustic phonons.

1. Introduction

Si and Ge are the basics materials of nano- and optoelectronics, vital elements of CMOS (complementary metal-oxide- semiconductor) technology – the most widely applied semiconductor technology worldwide[1]. After decades of growth following Moore’s low, semiconductor industry, finally, starts to slow down because of the principal physical limitation of semiconductor-based electronics[2]. The crucial points are speed and density of signal transmission as well as thermal overheating and power consumption. One of the idea to overcome these challenges is to use light as a signal carrier [3]. However, taking to account well-developed CMOS technology processes and a massive amount of the investment already made to this industry, the new nanoelectronics technological processes must be compatible with CMOS production. This approach challenged already scientific minds over the last decade and got the name of “Silicon photonics” [3][4][5]. Unfortunately, because of the indirect bandgap structure of Si and Ge, they are naturally pure light emitters, because Auger recombination and free carrier absorption dominate over photon emission in these materials[1].
However, it was already shown, the tensile strain in Ge thin film initiates changes in band structure and facilitates direct-gap recombination[6]. The other way to modify Ge band structure is the addition of Sn [7][8]. The Sn content decreases bandgap width, more for the Γ- than for the L-valley. As a result, GeSn alloys became a direct bandgap material. However, the concentration of Sn in the alloy is limited by precipitation of Sn. One of the ways to increase concentration is the usage of thin (pseudomorphic) alloy layers. In order to enlarge the active volume of possible photonics devices, periodic structures of thin layers, like superlattice, could be used. Moreover, it was as well reported, the quantum confined nanostructures like quantum wells demonstrate increased photon emission thanks to stimulated electron-hole pair formation promoted by the limited carrier path length. [9]

Raman spectroscopy is one of the well-established methods for determining mechanical stress of materials while the change in lattice constant caused by the stress can be detected as a shift in phonons spectral position. The compositional changes in alloys also influence the lattice constant as well and modify the position and relative intensity of Raman spectral lines [10][11]. It has been already demonstrated in the literature[12][13], that in case of Ge,Si./Si superlattice, one can derive Ge composition (x) from the comparison of the measured acoustic phonon mode frequencies with those theoretically calculated by the elastic continuum model[14] assuming a linear relationship between sound velocity in Ge,Si./, and x. This makes Raman spectroscopy a promising method for analysis of stress and composition in GeSiSn alloys.

In this study, we discuss the possibility to determine Sn concentration in periodical GeSiSn/Si nanostructures or superlattices (for phonons) from the analysis of Raman spectra measured in acoustic and optical spectral regions. In case of optical phonons, in contradiction with the literature data for single layer GeSiSn[10][11], we did not observe pronounced changes of longitudinal optical (LO) modes with Sn concentration. This could be explained by compensation of the high-frequency Raman shift induced by a compressive strain in the film plane[15] with a low-frequency Raman shift caused by phonon confinement effect in thin GeSiSn layer(quantum well)[16].

In the case of the acoustic spectral region, we observe the doublets of the folded longitudinal acoustic (FLA) phonons, the frequency position of which changes with Sn content variation. However, the usage of a linear relationship between a sound velocity in GeSiSn layers and Sn content fails to explain the experimentally observed FLA phonon mode frequencies and to determine Sn content. This requires exact information on the dependency of the sound velocity in GeSiSn layers as a function of Sn content from independent measurements.

2. Experimental
The growth of pseudomorphic GeSiSn layers was realized by molecular beam epitaxy in ultrahigh vacuum conditions at 10^-7 – 10^-8 Pa using the “Katun C” system (Institute of Semiconductor Physics, Novosibirsk). The electron beam evaporator and the corresponding Knudsen effusion cells were used for Si, Ge, and Sn deposition, respectively. First, the Si(100) substrates were covered with 150 nm Si buffer layer at 700°C. Then, ten layers of 2 nm GeSiSn film(grown at 150 °C) with 10 nm of Si on top ( grown at 460 °C) were deposited. Finally, 40 nm-thick Si protection layer was deposited on the top of the structure. The Ge content was fixed at 30%, while the Sn content was varied from 0 to 20%.

Raman spectra were measured in the z(xy)-z and z(xx)-z backscattering geometries at room temperature using a triple spectrometer T64000 (Horiba Jobin Yvon, France) equipped with a confocal microscope, and liquid nitrogen cooled charge coupled detector. The excitation line of Ar+ ion laser with the wavelength of 514.5 nm and the power 1.4 mW at the sample surface was used in the Raman experiments. The spectral resolution was set 4 cm\(^{-1}\).

3. Result and discussion
Fig.1a demonstrates typical Raman spectra of the samples under investigation. According to Raman selection rules, only LO phonons can be observed in the z(xy)-z scattering geometry. The spectral lines assigned to Ge-Ge and Ge-Si optical vibrational modes are clearly seen at 300 and 420 cm\(^{-1}\), respectively [10]. An intense peak at 520 cm\(^{-1}\) is due to Si-Si vibration modes of a bulk Si substrate and Si layers.
Note, that our measurements reveal negligible changes in the mode position vs. Sn content. This is in contradiction with Refs[10], [11] which demonstrate a linear low-frequency shift of Ge-Ge and Si-Si modes with Sn concentration change from 0 to 11%. One of the possible explanation of such behavior could be a combination of the influence of compressive stress induced by the lattice mismatch between GeSiSn layer and Si buffer layer and the phonon confinement effect in a 2 nm-thick GeSiSn layer. These effects lead to spectral shifts of Raman mode in opposite directions and, most probable, compensate each other[12]. This makes it challenging to determine Sn concentration from the analysis of the frequencies of optical phonons observed in the Raman spectra.

On the other hand, the periodicity of the superlattice with the layer thickness smaller than 1/q, where q is wavevector in the Brilliouin zone of bulk material, leads to the formation of Brillouin minizone and appearance of FLA phonons. The resulting acoustic phonon dispersion can be obtained by the folding of the original dispersion curve into the minizone. The acoustic phonon dispersion curves in the structures like Si/SiGe and thus the doublet frequency positions observed in the experiment were calculated in [13] by using the elastic continuum model[14]:

\[
\cos(qd) = \cos(\frac{\alpha_1}{\nu_1})\cos(\frac{\alpha_2}{\nu_2}) - \frac{K^2 + 1}{2\kappa}\sin\left(\frac{\alpha_1}{\nu_1}\right)\sin\left(\frac{\alpha_2}{\nu_2}\right)
\]

where \(\kappa = \nu_1\rho_1 / \nu_2\rho_2\), and \(d = d_1 + d_2\); \(d_1\) and \(d_2\), \(\rho_1\) and \(\rho_2\), \(\nu_1\) and \(\nu_2\) are the thickness, density and sound velocity in Si, Ge and Sn layers, respectively. The same approach can be applied to our samples.

In the z(xx)-z scattering geometry for GeSiSn/Si superlattices optical phonons are forbidden, while the FLA phonons become active. Fig.1b shows the acoustic part of the Raman spectra of GeSiSn/Si superlattices with Sn concentration varied from 3.5 to 20%. Up to 3rd FLA doublet can be seen in the Raman spectra. One can clearly see that the FLA doublet positions undergo a low-frequency shift with increasing the Sn concentration. This demonstrates the sensitivity of acoustics phonons to Sn addition. In order to model GeSiSn layer properties, we applied model (1) for our Ge_{0.3}Si_{0.7-x}Sn samples using \(\rho_1 = 0.3\rho_{Ge} + (0.7-x)\rho_{Si} + x\rho_{Sn}\) and \(\nu_1 = 0.3\nu_{Ge} + (0.7-x)\nu_{Si} + x\nu_{Sn}\). Density and sound velocity of bulk Si, Ge and Sn was taken from [13] and [17] respectively.

The typical calculated dispersion curve for the FLA phonons is presented on Fig.2a. In our case, the excitation wavelength \(\lambda_1 = 514.5\) nm, and the wavevector \(q = 4\pi/\lambda_1 = 1.054 \times 10^6\) sm\(^{-1}\), where the refractive index n=4.33 for Ge and Si. For Sn the refractive index n=2, taking to account that maximum amount of Sn is 20%, a variation of n should not be more than 10%, and normalized wavevector \(q/\pi/d\) determined as 0.4±0.04.

The model (1) demonstrates a shift in the range of 1.5 cm\(^{-1}\) with Sn concentration change from 0 to 20%. Meanwhile, the experimentally observed spectral shift was at the range of 4-5 cm\(^{-1}\). This confirms the limitation of linear dependence of sound velocity and Sn content for our samples.

In order to fit experimental spectra, the density of the GeSiSn layer was fixed at 3.21x10\(^3\) g/cm\(^3\), because the density variation causes negligible changes in the dispersion curves. We varied only sound velocity in a way, the resulted dispersion curve fits the measured spectra. Fig. 2b demonstrates sound velocities obtained from the best fit of the calculated doublets to the experimental FLA phonon frequencies for samples under the study. One can see a nonlinear dependency of sound velocity on the Sn content. Having the sound speed velocity dependency, one can control Sn concentration in GeSiSn layer by Raman spectroscopy in the acoustic spectral region by using the elastic continuum model. However, to estimate Sn concentration from the frequency position of the FLA doublets for GeSiSn/Si superlattices investigations of sound velocity in GeSiSn alloys by independent methods are required.

4. Conclusion
We apply Raman spectroscopy to study the phonon response of GeSiSn/Si superlattices. The position of LO phonons could be explained with the opposite shifts induced by compressive stress in the GeSiSn
film and confinement effect. We demonstrate the sensitivity of acoustics phonon dispersion to the concentration of Sn in GeSiSn/Si superlattice. According to our knowledge, it is the first time demonstration of such behavior in GeSiSn/Si superlattices. The modeling of phonons behavior by the elastic continuum model reviles a nonlinear dependency of GeSiSn sound velocity and requires further detailed measurements. Our study opens the new way of the Sn content control in GeSiSn/Si periodical nanostructures.

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Fig. 1 a) Raman spectra of Ge$_{0.3}$Si$_{0.5}$Sn$_{0.2}$/Si superlattice measured in different geometries. The inset to the figure shows the acoustic spectral range. b) Acoustic part of Raman spectra for the samples with Sn concentration 3.5, 6, 1, 14 and 20% (from bottom to top).
Fig. 2  a) The typical dispersion curve for the FLA phonons obtained for Ge$_{0.3}$Si$_{0.5}$Sn$_{0.2}$/Si superlattices calculated using the elastic continuum model. The horizontal line indicates the wavevector used in the experiment. b) Calculated sound velocity of GeSiSn layer vs. Sn content.