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Study of the band structure of GeSiSn/Ge/Si heterostructures by FTIR photoreflectance spectroscopy

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Abstract. The work demonstrates the use of photomodulation FTIR spectroscopy to study structures containing epitaxial layers of GeSn and GeSiSn in the temperature range of 79–180 K. The photoreflectance method has enabled observation of direct interband transitions, and evaluation of the impact of temperature variation and mechanical strain on their energy values.

Keywords: semiconductors, solid solutions, FTIR spectroscopy, photoreflectance method, heterostructures, silicon, epitaxy

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Исследование зонной структуры гетероструктур GeSiSn/Ge/Si методом инфракрасной фурье-спектроскопии фотоотражения

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Аннотация. В работе продемонстрировано применение метода фотомодуляционной ИК фурье-спектроскопии для исследования структур, содержащих слои GeSn и GeSiSn в диапазоне температур 79–180 K. Метод фотоотражения позволил наблюдать прямые межзонные переходы, оценить влияние температуры и механических напряжений в структуре.

Ключевые слова: полупроводники, твердые растворы, фурье-спектроскопия, метод фотоотражения, гетероструктуры, кремний, эпитаксия

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Introduction

Presently there is an active interest in research on the development of semiconductor devices based on group IV compounds of the periodic table (Si, Ge and Sn). Such compounds can have a direct band structure, which makes it possible to create light-emitting devices on their basis. Another important advantage is its good compatibility with silicon technology [1, 2]. One promising alloy is $Ge_{1-x}Sn_x$, which has a direct band structure at a certain tin content (from about 6.5–8.6 % [3, 4]). This makes it possible to manufacture photodetectors and light-emitting devices, such as lasers and LEDs, in the mid-infrared wavelength range based on this compound. Studies [5, 6] have attempted to create a photodiode and an LED based on such an alloy. Another promising compound for these purposes is the $Ge_{1-x-y}Si_xSn_y$ alloy, which enables band engineering through the adjustment of the Sn content [3]. The possibility of obtaining emitting and photodiode structures based on this alloy has also been demonstrated [7–9].

The goal of the current work is to obtain information about the band structure of the $Ge_{1-x-y}Si_xSn_y$ alloy using the FTIR photoreflectance spectroscopy method. Knowledge of the band structure parameters of $Ge_{1-x-y}Si_xSn_y$ can be used for the development of new optoelectronic devices.

Materials and Methods

In this study, the optical properties of heterostructure samples containing $Ge_{0.918}Sn_{0.082}$ and $Ge_{0.923}Si_{0.025}Sn_{0.052}$ alloys were investigated. The samples were grown via molecular beam epitaxy on (100) silicon substrates. The studies were performed using two series of structures. As the base of the samples of each series, a 100 nm silicon buffer layer was grown on a silicon substrate, on top of which, after a 10 nm $Ge_{0.3}Sn_{0.7}$ insert, a 200 nm thick Ge virtual substrate layer was formed. The final layer, 200 nm thick, was different for each series of samples: $Ge_{0.918}Sn_{0.082}$ for series A; $Ge_{0.923}Si_{0.025}Sn_{0.052}$ for series B. For each series, the samples were annealed in an argon atmosphere at different temperatures (see Table).

Table

Description of the studied samples

Annealing temperature	Non-annealed	125 °C	300 °C	350 °C
Series A	A0	A1	A2	A3
Series B	B0	B1	B2	B3

To study the optical properties of the samples described above, the method of photomodulation Fourier-transform infrared (FTIR) spectroscopy was used. The photoreflectance method is based on measuring the changes in the intensity of the probe beam as a result of the periodic action of the modulating beam ($\hbar\omega > E_g$) on the electric field within the sample. Photoinjected electron-hole pairs are separated under the influence of this field and partially compensate for the surface charged states. This causes a change in the optical characteristics of the structure and, consequently, leads to modulation of the reflectance. Using phase-sensitive detection, a change in the reflection coefficient is recorded, which can be either positive or negative, depending on the phase of the reflectance modulation [10].

The experimental setup was based on a Vertex 80 FTIR spectrometer equipped with CdHgTe and InSb photodetectors cooled by liquid nitrogen. Synchronous detection was performed by

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using an SR-830 lock-in amplifier. Light from an incandescent lamp with a quartz bulb was used as a probe beam, and modulation was carried out by a laser with a wavelength of 405 nm, which was mechanically chopped at a frequency of 2.3 kHz. To cool the samples, a liquid-nitrogen-cooled cryostat and a closed-cycle helium cryostat were used, allowing a cooling temperature down to 11 K to be achieved.

During the preparation of the spectra for analysis, a phase-correction technique was used to restore the modulation phase [11]. The photoreflectance spectra were analyzed using the method described previously [12].

Results and Discussion

For the first series of samples containing a $Ge_{0.918}Sn_{0.082}$ layer, the photoreflectance spectra measured in the temperature range of 79–180 K are presented in Fig. 1. For all the samples a photoreflectance signal in the form of a double peak is present on the left side of the spectrum. The left maximum corresponds to a direct interband transition in the $Ge_{0.918}Sn_{0.082}$ compound. The nature of the right extremum at the time of writing the work is not clear, but we assume that the double peak may appear because of the presence of mechanical strain in the structure. Such strain can cause a splitting in energy between the subbands of heavy and light holes. This assumption correlates with the results of X-ray diffraction measurements, which have given the strain relaxation degree of only 72% for the $Ge_{0.918}Sn_{0.082}$ epitaxial layer.

For the A0 and A1 samples, additional photoreflectance signals in the spectra were observed at energies above 800 meV. These evidently belong to the germanium virtual substrate layer, as their energy corresponds to the direct interband transition in this material.

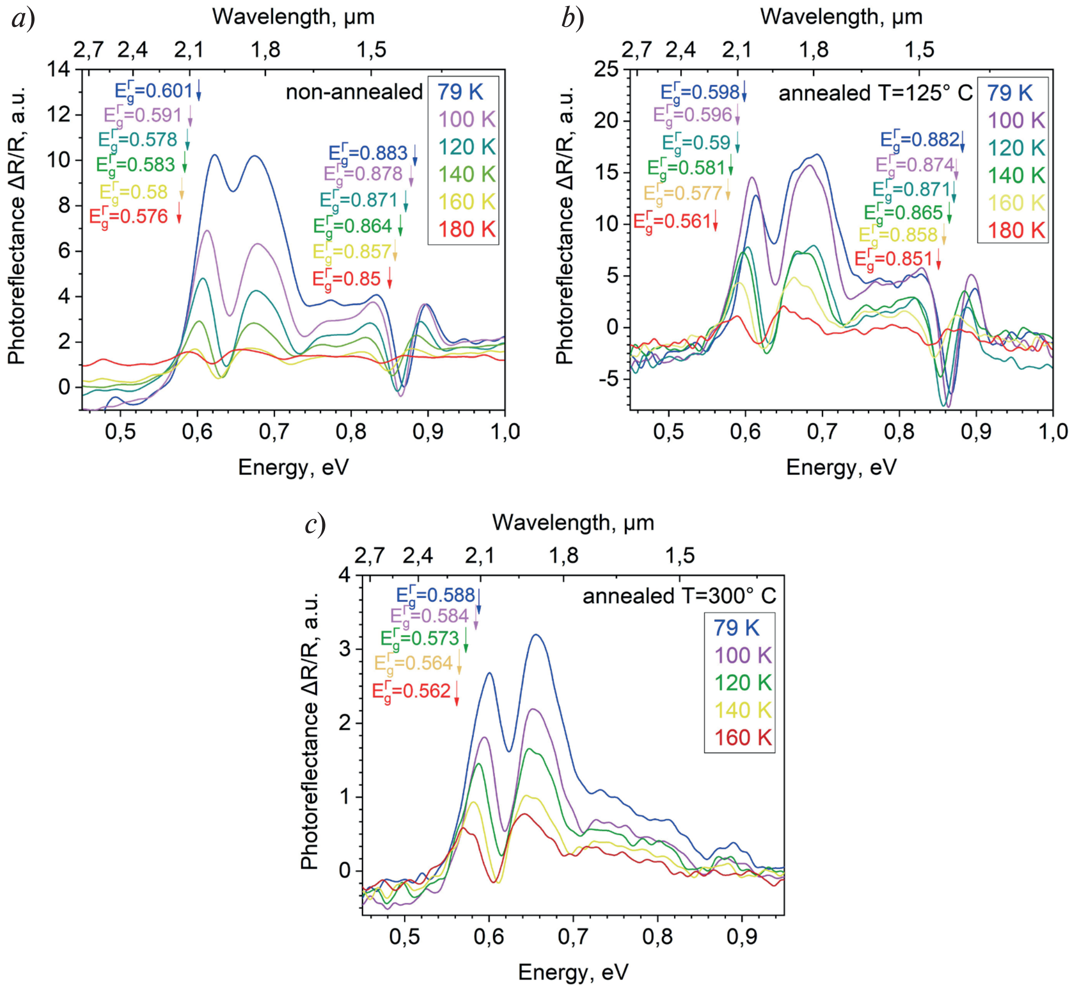

Fig. 1. Photoreflectance spectra for samples of series A: non-annealed, A0 (*a*); annealed at 125 °C, A1 (*b*) and annealed at 300 °C, A2 (*c*)

From the spectra of the Series A samples, one can also evaluate the effect of annealing on the photoreflectance signal. For example, it can be noted that the signal from sample A1 is increased compared to non-annealed one (A0). With further annealing, the signal began to weaken and was not observed for sample A3. Presumably, the annealing changes the concentration of defects and therefore the equilibrium concentration of charge carriers, which affects the built-in electric field of the sample, resulting in a weaker reflectance modulation.

Fig. 2 shows the temperature dependences of the energy of the direct transitions in the $Ge_{0.918}Sn_{0.082}$ layer (*a*) and germanium layer (*b*), obtained from the analysis of the spectra using the techniques described in [12]. The experimental results were approximated by the empirical Varshni equation, and the fitting parameters for each sample are shown as insets in the corresponding figures. In comparison, the corresponding dependences were plotted based on the available literature [13–16]. By comparing the experimental results for Ge with the literature data in Fig. 2, *b*, a good accuracy of the photoreflectance method for studying such structures is shown.

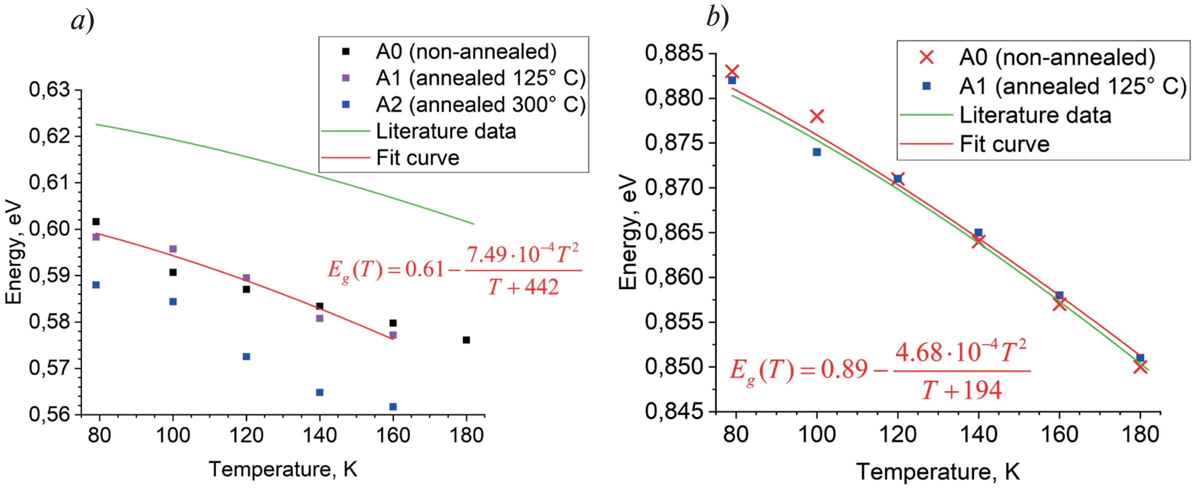

Fig. 2. Temperature dependence of the energy of direct transitions in the $Ge_{0.918}Sn_{0.082}$ (*a*) and Ge (*b*) layers

According to the dependencies in Fig. 2, *a*, it can also be noted that the experimentally obtained energy values for $Ge_{0.918}Sn_{0.082}$ do not precisely coincide with the calculations based on literature data. This discrepancy can be explained by the presence of mechanical strain in the structure. In addition, for the sample A2 annealed at 300 °C, the energy value at 79 K was lower by ~12 meV relative to A0 and A1. Along with the observed greater splitting of the photoreflectance peak, this may imply a change in the strain values in the case of annealing at a relatively high temperature.

The photoreflectance spectra of the sample series with the $Ge_{0.923}Si_{0.025}Sn_{0.052}$ epitaxial layer are shown in Fig. 3, *a*. The spectra exhibited a broadened and asymmetrical (relative to the maximum) peak, which can be represented as a combination of two signals. Indeed, at energies less than 770 meV, signals from the $Ge_{0.923}Si_{0.025}Sn_{0.052}$ alloy are observed, from which the values of the energy gap at the Γ point are determined. The broad shoulder to the right of the maximum is likely caused by the signal from the Ge virtual substrate, which was observed in the samples of series A.

The dots in Fig. 3, *b* indicate the temperature dependence of the value of the direct transition energy in $Ge_{0.923}Si_{0.025}Sn_{0.052}$ obtained from the analysis of the photoreflectance spectra. The red curve approximates the experimental data using the Varshni equation, and the green curve is a dependence constructed on the base of literature data [13–16]. Notably, in this series of samples, the photoreflectance signal was observed only for the non-annealed sample. The absence of the signal in the annealed samples can be caused by a decrease in the modulation of the built-in electric field. Additional research would be necessary to determine the reason behind this effect.

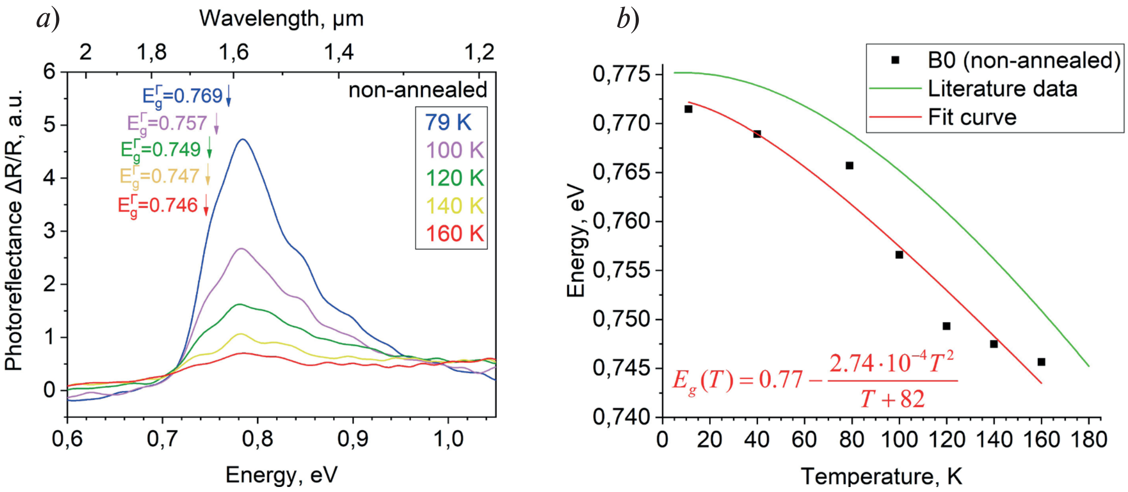

Fig. 3. Photoreflectance spectra for the sample B0 (*a*) and temperature dependence of the obtained energy of direct transitions in the $Ge_{0.923}Si_{0.025}Sn_{0.052}$ layer (*b*)

Conclusion

The FTIR photoreflectance spectroscopy method was employed to study the band structure of $Ge_{0.918}Sn_{0.082}$ and $Ge_{0.923}Si_{0.025}Sn_{0.052}$ epitaxial layers. The photoreflectance spectra of $Ge_{0.923}Si_{0.025}Sn_{0.052}$ were detected for the first time. An analyzis of the spectra made it possible to study the energy gap at the Γ point in the $Ge_{0.918}Sn_{0.082}$ and $Ge_{0.923}Si_{0.025}Sn_{0.052}$ alloys. For the non-annealed samples, the energy values of direct transitions at a temperature of 79 K were 801 meV for $Ge_{0.918}Sn_{0.082}$, and 769 meV for $Ge_{0.923}Si_{0.025}Sn_{0.052}$. Based on the temperature dependence of photoreflectance, the change in the energy values of interband transitions was estimated, and an increase in mechanical stress with increasing temperature was shown. The information obtained about the samples demonstrates the good applicability of the photoreflectance FTIR spectroscopy as a method of investigating the band structure of epitaxial $Ge_{1-x-y}Si_xSn_y$ alloys.

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