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Investigation of the effect of annealing and composition on infrared photoluminescence of GeSiSn/Si multiple quantum well nanoheterostructures

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The results of studying the photoluminescence of nanoheterostructures with multiple $Ge_{1-x-y}Si_xSn_y$/Si quantum wells grown by molecular beam epitaxy on silicon substrates and annealed at different temperatures are presented. As a result of the annealing of the structures, a multifold increase in the intensity of the luminescence peak close in energy to the optical transitions within the multiple quantum wells is observed. The optimal annealing temperature and duration are determined in terms of the intensity of photoluminescence. The luminescent properties of a series of annealed $Ge_{0.93-x}Si_xSn_{0.07}$/Si structures with different Ge compositions are investigated. As a result, a shift of the low-temperature photoluminescence peak towards lower energies with an increase in the fraction of germanium in the alloy composition is shown. Thus, the possibility of controlling the luminescence spectrum of $Ge_{0.93-x}Si_xSn_{0.07}$/Si nanoheterostructures in the wavelength range of 1.3−2.0 μm is demonstrated.

Keywords: nanoheterostructures, photoluminescence, molecular beam epitaxy, infrared emitters.

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1. Introduction

Presently, active studies are undergoing to create semiconductor compounds based on the 4-group elements (Si, Ge and Sn), since these compounds enable implementing silicon-compatible devices designed to operate in the near- and mid-infrared ranges [1,2]. One promising material for manufacturing the emitters and the photodetectors for the mid-IR range is the GeSn alloy, which, in accordance with the theoretical calculations, has a direct-band structure at the tin content of 6.5−10% [3,4]. This material has been already used as a base to manufacture the p-i-n-photodetectors [5], light-emitting diodes [6] and lasers with the optical [7] as well as electric pumping, designed to emit at the wavelength of 2.3 μm [8]. At the same time, GeSn has certain disadvantages, as the high tin content results in its segregation, thereby inevitably leading to the increase in the number of the defects and complicating the controllable growth of such structures [9]. The big mismatch of the lattice constants ($\sim 15\%$) requires selection of the optimum ratio between Ge and Sn for producing pseudomorphic layers on the Si-substrates.

An alternative to GeSn can be application of the GeSiSn alloy similar to Si in terms of the lattice constant, thereby offering wide possibilities for the creation of photonic devices. Currently, it is possible to produce the emitting and photodetector structures based on GeSiSn, which are grown on the germanium buffer layer of a large thickness [10,11]. However, such structures contain quite a big number of dislocations, while by varying the composition of $Ge_{1-x-y}Si_xSn_y$, it is possible to grow dislocation-free stressed layers on silicon. Due to the small critical thickness of the pseudomorphic growth of the ternary $Ge_{1-x-y}Si_xSn_y$ alloy, it is preferable to create emitting structures on its basis by forming quantum wells. In particular, the studies [12,13] have theoretically examined the $Ge_{1-x-y}Si_xSn_y/Ge_{1-x}Sn_x$ heterostructures, used as an example to predict the possibility of manufacturing infrared laser diodes with the emission wavelength of 1.55 and 2.3 μm.

We have proposed and implemented in practice an original approach to creating emitting structures on the silicon substrate, which consists in forming multiple $Ge_{1-x-y}Si_xSn_y$/Si quantum wells (MQW) by the molecular beam epitaxy (MBE) [14]. The previous studies [14,15] have shown that these structures exhibit luminescence in the mid-wave IR range (1.55−3.3 μm). In our recent study [16] we have optimized the parameters of the epitaxy of the heterostructures with the $Ge_{0.3}Si_{0.63}Sn_{0.07}$/Si MQWs, including the rate and the temperature of their growth. This study has also found that the luminescent properties of these structures can be substantially affected by annealing, the usage of which enabled, in particular, revealing the dependence of the photoluminescence signal on the thickness of the narrow-bandgap layers.

The present study is dedicated to the more detailed study of the influence of annealing and the composition of the alloy on the photoluminescent properties of the structures based on the multiple $Ge_{1-x-y}Si_xSn_y$/Si quantum wells, and to selection of their optimum parameters in terms of luminescent characteristics.

2. Samples and experimental procedure

The study has investigated the nanoheterostructures with the multiple $Ge_{1-x-y}Si_xSn_y$/Si quantum wells, which are grown by the molecular beam epitaxy in the Katun' setup under an ultra-high vacuum of $10^{-7}-10^{-8}$ Pa. The silicon was sourced from an electron-beam evaporator, while germanium and tin were sourced from the Knudsen effusion cells [17]. The growth was controlled by the reflection high-energy electron diffraction. The layer arrangement in the produced nanoheterostructures is schematically shown on Fig. 1. The growth was performed on the silicon substrates of the (100) orientation with the buffer layer of the epitaxial silicon of a 150 nm thickness. The 10 periods of the alternating layers of $Ge_{0.93-x}Si_xSn_{0.07}$ and Si were grown on the buffer layer, while the thickness d of the narrow-bandgap $Ge_{0.93-x}Si_xSn_{0.07}$ layers was 1, 2 or 3 nm. The thickness of the silicon layers between the quantum wells was 7 nm. In order to study the influence of the composition of the ternary alloy on the photoluminescence, we have produced the nanoheterostructures with the same MQW thickness ($d = 1$ nm) and the various nominal content of germanium in the narrow-bandgap part: 30, 40, 50 and 78%.

The photoluminescence (PL) spectra of the studied structures were obtained by means of the measurement setup [18] based on the VERTEX 80 and Fourier-transform infrared spectrometer the closed-cycle CCS-150 helium cryostat. The optical pumping was performed by means of a semiconductor laser with the wavelength of 405 nm. The detection was performed by the InSb photodetector being cooled by liquid nitrogen. The PL signal was amplified by means of the SR-830 lock-in amplifier adjusted to the exciting laser modulation frequency of 2.5 kHz.

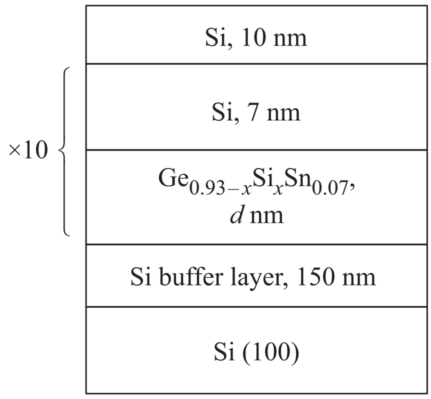

Figure 1. Diagram of the layer arrangement in the structure of the studied samples, where d is the thickness of the narrow-bandgap layer, and x is the content of silicon in the alloy.

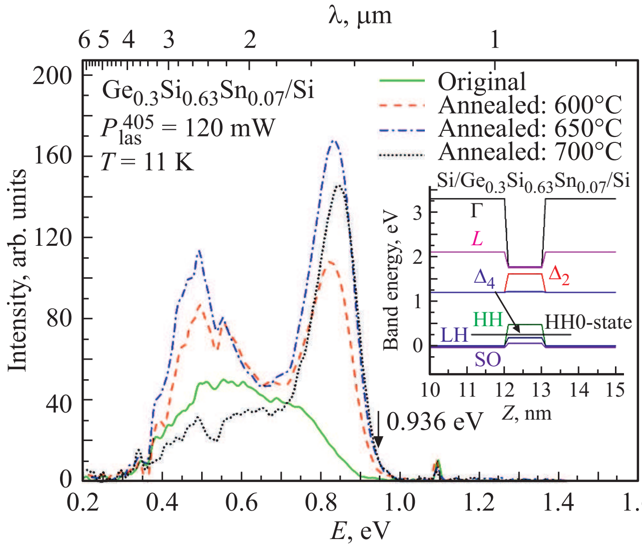

Figure 2. Dependence of the photoluminescence spectra of the structure with the multiple $Ge_{0.3}Si_{0.63}Sn_{0.07}$/Si quantum wells on the annealing temperature. The annealing time was 30 minutes. The arrow indicates the calculated energy of the MQW transitions. The insert shows the arrangement of the energy bands in the $Ge_{0.3}Si_{0.63}Sn_{0.07}$/Si quantum well, which is calculated in the study [16].

3. Results and discussion

The studied samples were annealed at the different temperatures in order to reduce the influence of the defects on their luminescent properties. The annealing was performed in the argon atmosphere at the temperatures 600, 650 and 700°C. The typical dynamics of transformation of the PL spectra with the annealing temperature is shown on Fig. 2 by the example of the structure with the 1-nm thickness of the $Ge_{0.3}Si_{0.63}Sn_{0.07}$ layers.

The PL spectrum of the initial unannealed sample exhibits a wide luminescence band within the energy range from 0.35 to 0.9 eV, while the annealing results in its splitting into two distinctly separate peaks. The long-wavelength peak, observed within the energy range from 0.35 to 0.65 eV with the maximum at ~ 0.5 eV, is substantially lower by the energy than the calculated bandgap $E_g = 0.75$ eV for the stressed $Ge_{0.3}Si_{0.63}Sn_{0.07}$ [17]. In order to reveal the nature of this peak, we have examined the PL temperature dependence for the studied structures [16]. The spectra did not exhibit the shift of the this signal when changing the measurement temperature from 11 to 220 K. At the same time, the analysis of the power dependences revealed a sublinear increase in the PL intensity with the increase in the pumping power. Along with the position of the luminescence band substantially below E_g, the listed features of the spectrum indicate the radiative recombination involving the defects, probably, via complexes appearing in the $Ge_{0.3}Si_{0.63}Sn_{0.07}$ alloy, which are formed with involvement of the vacancies (similar to the „tin–vacancy“ complexes in silicon [19], Position of the MQW PL peak at the various thicknesses of the narrow-bandgap layers

Thickness of the narrow-bandgap layer, nm	PL peak position by energy, eV
1	0.83
2	0.72
3	0.68

whose typical localization energy is within the 0.3–0.6 eV range). Their photoluminescence increase due to annealing is correlated to the decrease in the concentration of the defects contributing to the nonradiative recombination. At the annealing temperature of 700°C, the intensity of this luminescence band is substantially decreasing, which can indicate the reduction of the concentration of the radiative defects of the corresponding type.

Within the short-wave range of the spectrum, the annealing distinctly results in a separate peak with the energy of ~ 0.83 eV, whose intensity increases with the increase in the annealing temperature up to 650°C. Taking into account that the peak position is close to the calculated energy values of the optical transition in the stressed $Ge_{0.3}Si_{0.63}Sn_{0.07}$/Si structure [16], this signal may correspond to the luminescence of the multiple quantum wells. This assumption is confirmed by comparison of the results for the series of the structures with the various thickness of the narrow-bandgap layer, which has demonstrated that this peak is shifted towards the lower energies with the increase in the thickness of the $Ge_{0.3}Si_{0.63}Sn_{0.07}$ layers from 1 to 3 nm (see Table). This result was examined in more detail in the study [16], which shows that this peak corresponds to the transitions in the second-type heterostructure, which occur between the Δ_4 subband in silicon and the level of heavy holes in the narrow-bandgap $Ge_{0.3}Si_{0.63}Sn_{0.07}$ layer, as it is shown on the insert of Fig. 2.

The increase in the intensity of the short-wave PL peak with the increase in the annealing temperature can be explained by reduction of the concentration of the point defects contributing to the nonradiative recombination in the layers of the structure. Fig. 2 also shows the slight shift of the MQW luminescence peak towards the shorter wavelengths with the increase in the annealing temperature. This shift might be caused by the reduction of the concentration of tin in the $Ge_{0.3}Si_{0.63}Sn_{0.07}$ layer due to Sn diffusion to the adjacent areas [20]. This effect resulting in the blurring of the heterointerfaces can also explain the drop of the MQW peak intensity at the high annealing temperature (700°C), thereby making the annealing temperature of 650°C an optimum one.

After that we have performed the experiments aimed at determining the optimum annealing time at the temperature of 650°C in terms of the intensity of the short-wavelength peak. The sample with the thickness of the $Ge_{0.3}Si_{0.63}Sn_{0.07}$ layers equal to $d = 1$ nm had been annealed for 5, 10, 15, 30 and 45 minutes (Fig. 3).

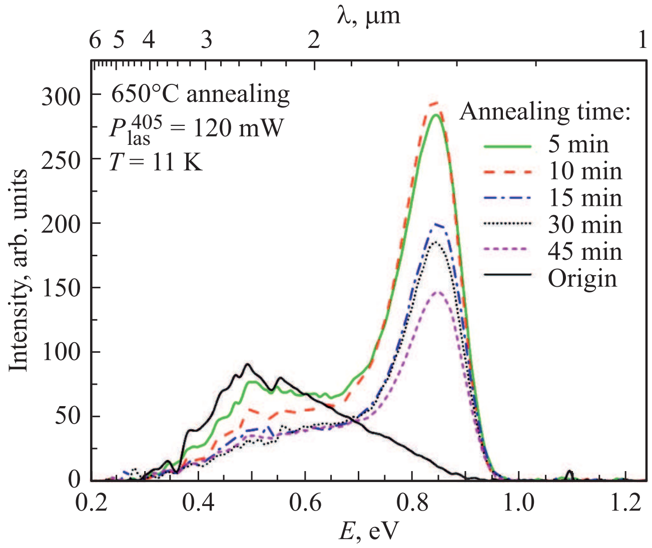

Figure 3. Photoluminescence of the sample with the 1 nm thickness of the $Ge_{0.3}Si_{0.63}Sn_{0.07}$ layer after annealing at the temperature of 650°C during 5, 10, 15, 30 and 45 minutes

The PL spectra have been compared to show that the short-wavelength peak in case of annealing for 5 and 10 minutes has almost the same intensity and at the same time it is 1.5 times more intense than in case of the annealing for 15 minutes. During the annealing for 30 and 45 minutes the intensity of this peak was only decreasing. The decrease in the intensity of the short-wavelength peak, which we attribute to the transitions in the $Ge_{0.3}Si_{0.63}Sn_{0.07}$/Si MQW, can be explained by the blurring of the heterointerfaces [20] due to such long annealing. The long-wavelength peak corresponding to luminescence of the defects has the maximum intensity in case of annealing for 5 minutes, while after the 10-minute annealing its intensity is decreasing in ~ 1.5 times. After annealing for 15 minutes, this peak decreases in ~ 1.5 times further and then its change is insignificant. Thus, it can be concluded that the optimum annealing time is 10 minutes: in this case the short-wavelength PL reaches the maximum intensity, while the peak of the radiative defects is noticeably reducing relative to it.

Next, the luminescent properties were compared for the series of the samples with the various content of Ge in the GeSiSn alloy. We have studied the samples with the Ge content of 30, 40, 50 and 78% (the thickness of the GeSiSn layers in the MQW was identical and equal to 1 nm), whose PL spectra are shown in Fig. 4.

The PL spectra of the initial unannealed samples had low intensity and a large full width at half-maximum (as illustrated in Fig. 4 by the spectrum of the structure with 50% of Ge before the annealing). These spectra exhibited a short-wavelength arm, which was shifted towards longer wavelengths with the increase in the Ge content. After the

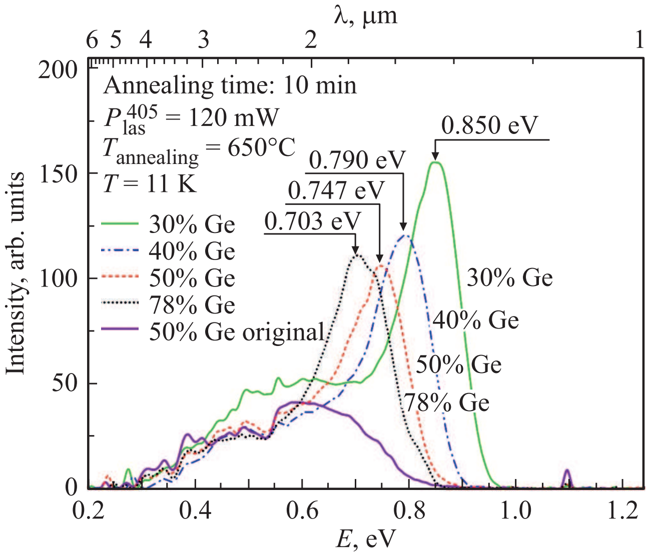

Figure 4. Photoluminescence of the samples with the Ge content of 30, 40, 50 and 78% after annealing at the temperature of 650°C for 10 minutes

annealing, all the samples exhibited a clear peak of photoluminescence of the $Ge_{0.93-x}Si_xSn_{0.07}$/Si MQW, which was shifted towards longer wavelengths with the increase in the Ge content in the alloy: 30% ~ 0.850 eV, 40% ~ 0.790 eV, 50% ~ 0.747 eV, 78% ~ 0.703 eV. Thus, the peak shift in wavelength was observed from 1.46 to 1.76 μm, while the total spectrum range of the MQW luminescence overlapped by these structures was 1.3–2.0 μm (see Fig. 4).

The intensity of the PL peak from the MQW for the sample with 30% Ge is 1.2–1.3 times higher than for the samples with 78, 50 and 40% Ge. It might be correlated to the fact that at the annealing for the structures with the larger Ge composition the temperature stability is less than for the samples with 30% Ge. The last conclusion is confirmed by the fact that during annealing for 30 minutes the intensity of the luminescence of the samples with 40 and 50% Ge becomes more than two times less than for sample with 30% Ge. Further on, it is planned to optimize the annealing parameters as well for the structures with the MQW with the germanium content of > 30%.

4. Conclusion

The study has investigated the photoluminescence of the multiple $Ge_{0.93-x}Si_xSn_{0.07}$/Si quantum wells grown on silicon substrates. It has been shown that the annealing of these structures allows multifold amplification of the PL peak corresponding to the transitions in the multiple quantum wells. The optimum time and the annealing temperature in terms of the intensity of the MQW luminescence peak have been determined to be 10 minutes and 650°C, respectively. It has been also shown that the annealing at the higher temperature of 700°C allows substantially decreasing the intensity of the luminescence band related to the structure defects. The PL studies of the series of the samples with the various Ge content in the GeSiSn alloy have demonstrated the substantial shift of the MQW PL peak towards smaller energies with the increase in the Ge composition thereby opening new perspectives for creating multi-layer structures emitting in the spectrum range of 1.3–2.0 μm.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] R. Soref. Nature Photonics, **4**, 495 (2010).
[2] C. Xu, L. Jiang, J. Kouvetakis, J. Menendez. Appl. Phys. Lett., **103**, 072111 (2013).
[3] K.L. Low, Y. Yang, G. Han, W. Fan, Y-C. Yeo. J. Appl. Phys., **112**, 103715 (2012).
[4] S. Gupta, B. Magyari-Kope, Y. Nishi, K.C. Saraswat. J. Appl. Phys., **113**, 073707 (2013).
[5] M. Oehme M. Schmid, M. Kaschel, M. Gollhofer, D. Widmann, E. Kasper, J. Schulze. Appl. Phys. Lett., **101**, 141110 (2012).
[6] Y. Zhou, W. Dou, W. Du, T. Pham, S.A. Ghetmiri, S. Al-Kabi, A. Mosleh, M. Alher, J. Margetis, J. Tolle, G. Sun, R. Soref, B. Li, M. Mortazavi, H. Naseem, S.-Q. Yu. J. Appl. Phys., **120**, 023102 (2016).
[7] S. Wirths, R. Geiger, N. von den Driesch, G. Mussler, T. Stoica, S. Mantl, Z. Ikonic, M. Luysberg, S. Chiussi, J.M. Hartmann, H. Sigg, J. Faist, D. Buca, D. Grützmacher. Nature Photonics, **9**, 88 (2015).
[8] Y. Zhou, Y. Miao, S. Ojo, H. Tran, G. Abernathy, J.M. Grant, S. Amoah, G. Salamo, W. Du, J. Liu, J. Margetis, J. Tolle, Y.-H. Zhang, G. Sun, R.A. Soref, B. Li, S.-Q. Yu. Optica, **7**, 924 (2020).
[9] P.R. Pukite, A. Harwit, S.S. Iyer. Appl. Phys. Lett., **54**, 2142 (1989).
[10] I. Fischer, T. Wendav, L. Auge, S. Jitpakdeebodin, F. Oliveira, A. Benedetti, S. Stefanov, S. Chiussi, G. Capellini, K. Busch, J. Schulze. Opt. Express, **23**, 25048 (2015).
[11] J.D. Gallagher, C. Xu, C.L. Senaratne, T. Aoki, P.M. Wallace, J. Kouvetakis, J. Menéndez. J. Appl. Phys., **118**, 135701 (2015).
[12] G. Sun, R.A. Soref, H.H. Cheng. Opt. Express, **18**, 19957 (2010).
[13] G. Sun, R.A. Soref, H.H. Cheng. J. Appl. Phys., **108**, 033107 (2010).
[14] V. Timofeev, A. Nikiforov, A. Tuktamyshev, V. Mashanov, M. Yesin, A. Bloshkin. Nanoscale Res. Lett., **13**, 65 (2018).
[15] V.A. Timofeev, V.I. Mashanov, A.I. Nikiforov, I.D. Loshkarev, I.V. Skvortsov, D.V. Gulyaev, I.V. Korolkov, D.V. Kolyada, D.D. Firsov, O.S. Komkov. Rus. Phys. J., **64**, 1505 (2021).

[16] V.A. Timofeev, V.I. Mashanov, A.I. Nikiforov, I.V. Skvortsov, A.E. Gayduk, A.A. Bloshkin, I.D. Loshkarev, V.V. Kirienko, D.V. Kolyada, D.D. Firsov, O.S. Komkov. Appl. Surf. Sci., **593**, 153421 (2022).
[17] V.A. Timofeev, A.I. Nikiforov, A.R. Tuktamyshev, V.I. Mashanov, I.D. Loshkarev, A.A. Bloshkin, A.K. Gutakovskii. Nanotechnology, **29**, 154002 (2018).
[18] D.D. Firsov, O.S. Komkov, V.A. Solov'ev, P.S. Kop'ev, S.V. Ivanov. J. Phys. D: Appl. Phys., **49**, 285108 (2016).
[19] L. Scheffler, M.J. Haastrup, S. Roesgaard, J.L. Hansen, A. Nylandsted Larsen, B. Julsgaard. Nanotechnology, **29**, 055702 (2018).
[20] N. von den Driesch, S. Wirths, R. Troitsch, G. Mussler, U. Breuer, O. Moutanabbir, D. Grutzmacher, D. Buca. Phys. Rev. Matter., **4**, 033604 (2020).