Material based on multilayer periodic structures with GeSiSn pseudomorphic layers

A.I. Nikiforov[*,1], V.A. Timofeev[1], V.I. Mashanov[1], I.D. Loshkarev[1], I.V. Skvortsov[1], D.V. Gulyaev[1], D.D. Firsov[2], O.S. Komkov[2]

[1]Rzhanov Institute of Semiconductor Physics SB RAS, Lavrentiev aven., 13, 630090, Novosibirsk, Russia
[2]Saint Petersburg Electrotechnical University (LETI), Prof. Popov str., 5, 197376, Saint Petersburg, Russia.

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* Corresponding author: e-mail: nikif@isp.nsc.ru, Phone: +7 383 330 4820, Fax: +7 383 330 7745

Изучен рост многослойных структур с гетропереходом $Ge_{0.3}Si_{0.7-y}Sn_y/Si$ при содержании олова от 0 до 18%. Методом рентгеновской дифрактометрии показано наличие строгой периодичности слоев и высокий уровень содержания олова. Установлено, что соединения GeSiSn являются термически стабильными в диапазоне температур отжига 300–550°C. От структуры с псевдоморфными слоями GeSiSn наблюдается сигнал фотолюминесценции в инфракрасном диапазоне около 3 мкм.

Ключевые слова: молекулярно-пучковая эпитаксия, Ge, Si, Sn, квантовые ямы.

The growth of multilayer structures with $Ge_{0.3}Si_{0.7-y}Ge_y/Si$ heterojunction at tin content from 0 to 18% was studied. The X-ray diffractometry method shows the presence of strict periodicity of layers and a high level of tin content. It has been established that GeSiSn compounds are thermally stable in the annealing temperature range of 300-550 °C. A photoluminescence signal in the infrared range of about 3 microns is observed from a structure with pseudomorphic GeSiSn layers.

Keywords: molecular beam epitaxy, Ge, Si, Sn, quantum well..

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I. Introduction

GeSiSn compounds are of interest for their use in multispectral imaging systems [1, 2], since they demonstrate a photoluminescence signal in the infrared wavelength of various ranges [3-8]. By changing the tin content in the GeSiSn solid solution layer, it is possible to adjust the band gap of the material and change the optical properties from the near to the far infrared range [9-11].

In order to advance into the infrared region, we suggest using materials based on Group IV elements (Ge, Si and Sn). The addition of Sn to the GeSi matrix allows for zone engineering. An increase in the tin content reduces the band gap and, thus, there is an increase in the operating wavelength from the near to far infrared range. In [6], the optical properties of multilayer GeSn/Ge heterostructures with compression deformations in GeSn layers were investigated and a mock-up of an IR photodetector was created, showing an increase in sensitivity in the entire range from 0.75 to 2.4 microns in comparison with a Ge-based photodetector. An increase in the photoresponse in the infrared range was observed in *p-i-n* diodes based on multilayer structures with pseudomorphic GeSiSn layers with an increase in the Sn

content from 0 to 14% [12]. Wirths and colleagues [13] reported on the creation of a mock-up sample of an optically pumped laser based on GeSn, and in [14] an electrically pumped laser based on GeSn was obtained for the first time, operating at a wavelength of 2.3 microns up to 100 K.

Despite the successes, there are still difficulties in the growth of GeSiSn materials. The main difficulties are associated with the segregation of tin [15]. Using the sputter epitaxy method, GeSn layers with tin content up to 11.5% were obtained without Sn segregation [16]. It was proposed to suppress the segregation effect by using a low-temperature buffer layer GeSn [17]. Another successful approach for obtaining GeSn layers with a high Sn content is to use thin layers of Sn with a thickness of several monolayers between Ge layers [18]. The maximum tin content was 15%. A similar approach was used in [19]. Firstly, an array of β-Sn tin islands was formed, and only then the a Ge layer was deposited and annealed. Here it was possible to achieve a tin content of up to 26%. Such layers allow you to move into the middle infrared region of 3–5 microns. The most interesting option from the point of view of zone engineering and thermal stability are the GeSiSn layers. Due to the increase in the entropy of mixing in the GeSiSn system compared to GeSn, the GeSiSn layers are more stable to thermal annealing [20].

The purpose of the work was to establish the regularities of the formation of the material based on GeSiSn compounds. In our work, we used pseudomorphic GeSiSn layers, since they do not contain defects, and obtained multilayer periodic structures with these layers on a Si substrate. A photoluminescence signal obtained from a material based on GeSiSn nanoheterostructures was observed in the infrared region.

II. Experiment

The material based on GeSiSn compounds was obtained by molecular beam epitaxy (MBE). and includes a multilayer periodic structure. Each period consists of a Si layer and a GeSiSn layer. The GeSiSn layers are in a pseudomorphic state. The MBE chamber is equipped with an electron beam evaporator for Si and Knudsen effusion cells for Sn and Ge for the synthesis of triple GeSiSn compounds with different compositions. After preliminary cleaning of the silicon surface from a thin layer of oxide, a buffer layer of Si with a thickness of 150 nm was applied to the Si(100) substrate at a deposition rate of 0.2 Å/c and at a growth temperature of 700°C to smooth the surface.

Next, a multilayer periodic structure was formed, in which the period consisted of a Si layer with a thickness of 7 to 23.5 nm and a GeSiSn layer with a thickness of 2 nm. The morphology and structure of the surface during growth were controlled by reflection high energy electron diffraction (RHEED). To determine the boundaries of the pseudomorphic state of the films, kinetic diagrams of the growth of GeSiSn films were established in the temperature range 100–300°C. The critical thickness was determined by constructing spatio-temporal intensity profiles along one of the directions in the RHEED picture.

The study of the stress state, composition and heterogeneities in structures with quantum wells was carried out by X-ray diffraction. To measure the diffraction reflection curves, a two-crystal X-ray diffractometer DSO-1T was used using a Ge(004) monochromator crystal in CuKα radiation (λ= 1.54056 Å). The phase analysis of the initial Sn films and tin oxides obtained after annealing was performed by X-ray powder diffractometry. It is an X-ray diffraction system (Shimadzu XRD-7000, CuKa radiation, λ = 1.54178 Å, linear detector OneSight) in the range of 2θ from 20° to 50°. The diffractograms were indexed using the PDF database (Powder Diffraction File, released in 2010, International Diffraction Data Center, Pennsylvania, USA). Optical properties were studied by photoluminescence (PL). The PL signal was recorded by a spectrometer with a cooled photoelectron multiplier with a photocathode S-20. In addition, the samples were pumped with a laser diode at a wavelength of 785 nm to observe PL in the mid-IR range. To achieve maximum efficiency in the mid-IR range, measurements were carried out using an InSb photodetector.

III. Results and discussion

The growth of structures containing quantum wells with pseudomorphic $Ge_{0.3}Si_{0.7-y}Sn_y$ films has been studied. At the first stage, multilayer periodic structures were obtained. They include elastically stressed $Ge_{0.3}Si_{0.7-y}Sn_y$ layers. Previously, we investigated kinetic growth diagrams of $Ge_{0.3}Si_{0.7-y}Sn_y$ layers with a tin content of less than 14% [8, 21]. Figure 1 shows a kinetic diagram of the growth of $Ge_{0.3}Si_{0.7-y}Sn_y$ layers on Si(100) with an Sn content of 14 and 18% in the temperature range of 100–300°C. An increase in the tin content makes it possible to move into the longer-wavelength infrared region of the spectrum, as discussed in the introduction.

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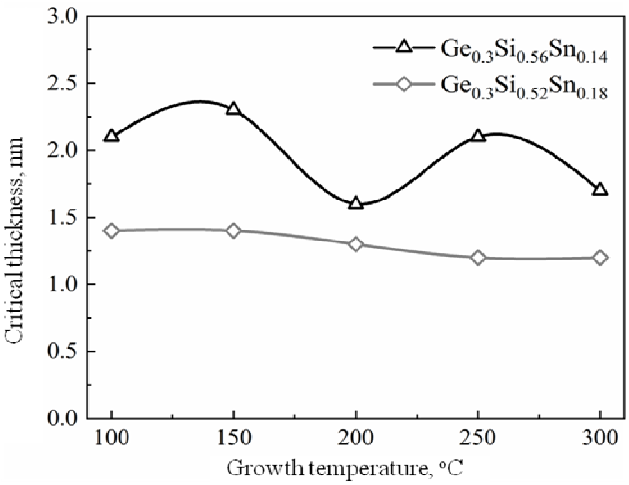


Figure 1. Kinetic growth diagram of $Ge_{0.3}Si_{0.7-y}Sn_y$ layers for Sn content 14 and 18%.

The region of existence of the pseudomorphic state of $Ge_{0.3}Si_{0.7-y}Sn_y$ films is located under the curve describing the critical thickness of the 2D-3D transition. The film exceeding the critical thickness of the 2D-3D transition represents an array of three-dimensional GeSiSn islands. The curve corresponding to the tin content of 14% has one minimum at 200°C and two maxima around 175 and 250°C. The higher temperature range from 200 to 300°C was well described by us in [21]. This area corresponds to a change in the mechanisms of two-dimensional film growth from two-dimensional islet growth to islet growth due to the movement of steps. The decrease in the critical thickness of the 2D-3D transition in the low-temperature region from 175 to 200°C can be explained by the influence of tin, which acts as a surfactant that accelerates the surface diffusion. The critical thickness of the 2D-3D junction varies from 1.5 to 2.5 nm in the studied temperature range.

The next curve, corresponding to the tin content of 18%, is straightened and the features associated with the change of mechanisms of two-dimensional growth are no longer observed. The values of the critical thickness vary slightly from 1.25 to 1.4 nm over the entire temperature range from 100 to 300°C. Such small values, first of all, can be associated with the ultimate solubility of tin in the GeSi matrix. An increase in the growth temperature above 300°C leads to segregation of tin and a solid solution of a given composition is not formed. This is fixed by the appearance of superstructures in the RHEED picture.

Phase diagrams describing superstructural changes in various tin coatings are shown in Fig. 2.

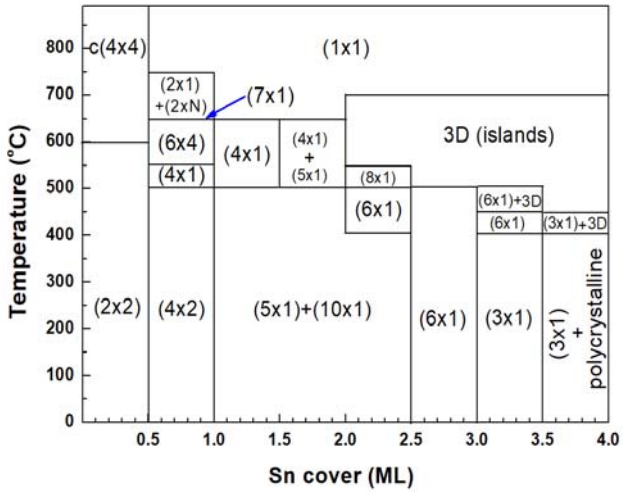


Figure 2. Phase diagram of the superstructural change during annealing of the Sn film on the Si(100) surface.

Based on kinetic growth diagrams of $Ge_{0.3}Si_{0.7-y}Sn_y$ films, the thickness region corresponding to the pseudomorphic state was selected. The advantage of such films in comparison with thick layers is the absence of dislocations in them. Knowledge of the region of existence of elastically stressed films makes it possible to choose the growth parameters of multilayer periodic structures containing up to ten periods with $Ge_{0.3}Si_{0.7-y}Sn_y$/Si heterojunction. The thickness of the $Ge_{0.3}Si_{0.7-y}Sn_y$ layer was chosen 2 nm for tin content up to 14% inclusive at a growth temperature of 150°C. The period included a $Ge_{0.3}Si_{0.7-y}Sn_y$ layer with a thickness of 2 nm and a Si layer with a thickness of 7 to 23.5 nm deposited on top of a solid solution layer at a temperature of 500°C. To avoid tin segregation, it was proposed to use two-stage Si growth. First, a low-temperature silicon layer was formed, and then the temperature rose to a final growth temperature of 500°C.

Figure 3 shows a RHEED picture during the growth of Si on top of the GeSiSn layer in the azimuthal direction [110] during the formation of a multilayer periodic structure. A superstructure (4×1) is observed, which corresponds to a tin coating at a temperature of 500°C [8]. Optimization of the growth of low-temperature and high-temperature silicon layers makes it possible to achieve minimal segregation of tin.

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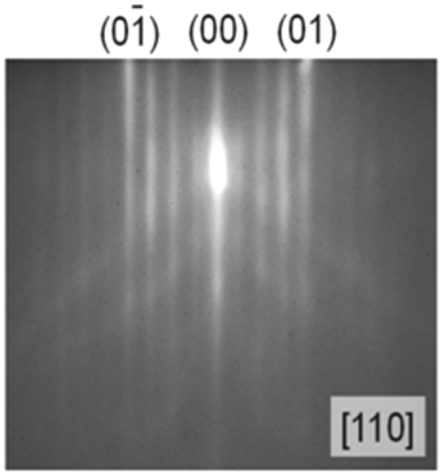


Figure 3. The RHEED pattern observed in the azimuthal direction [110] during the growth of Si on top of the GeSiSn layer during the formation of a multilayer periodic structure.

The stress state, composition, quality of heterogeneous boundaries and thermal stability of multilayer periodic structures were studied by X-ray diffractometry. In Figure 4, one can see the diffraction reflection curves (004) for samples with different tin content of 7 and 14%. The diffraction reflection curves are shifted along the intensity axis for clarity.

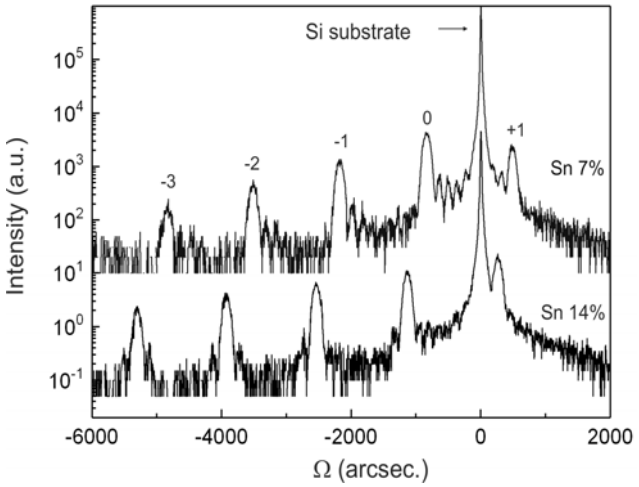


Figure 4. Diffraction reflection curves (004) from multilayer periodic structures with pseudomorphic GeSiSn films with a tin content of 7 and 14%.

They contain a peak from the Si substrate and satellites associated with the periodic structure of the samples. Satellites up to the 4-th order are observed, which indicates the high quality of the structure and strict periodicity. The position of the zero satellite corresponds to the average composition of the periodic structure. From the figure you can see the angular displacement of the zero sattelite for the tin content of 7 and 14%. The angular distance between the satellites depends on the thickness of the period. The thickness of the period was the same and was 14 nm: 2 nm thickness GeSiSn and 12 nm thickness Si.

The pseudomorphic state of the films is confirmed by the shape of the diffraction reflection curve. In addition to the composition, period and stress state, the thermal stability of the structures was studied during their annealing up to a temperature of 550°C (Fig. 5). A structure with a tin content of 7%

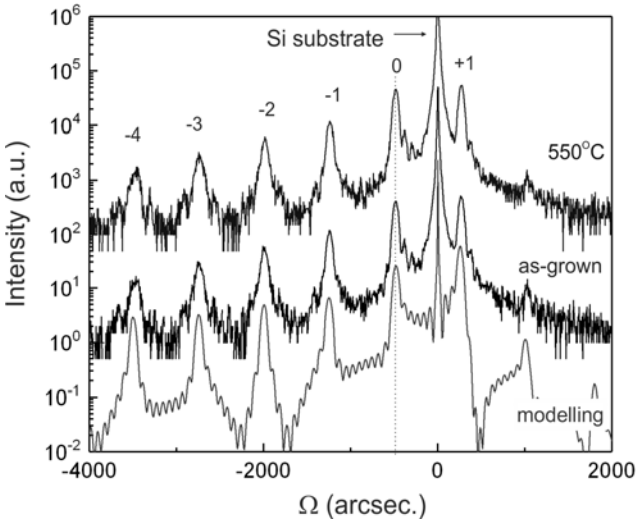


Figure 5. Diffraction reflection curves (004) from multilayer periodic structures with pseudomorphic GeSiSn films with a tin content of 7% for as-grown sample and for the sample annealed at 550° C and a simulation of the curve corresponding to as-grown sample.

in $Ge_{0.3}Si_{0.7-y}Sn_y$ layers was used. This composition was confirmed by the data of diffraction reflection curves. The period consisted of a $Ge_{0.3}Si_{0.7-y}Sn_y$ layer with a thickness of 2 nm and a Si layer with a thickness of 23.5 nm. Following the position of the zero sattelite for both the initial sample and annealed at 550°C, it can be concluded that annealing of the sample does not change its average composition. The curves were modeled using Sergey Stepanov's X-ray Server resource (https://x-server.gmca.aps.anl.gov /).

The optical properties of multilayer periodic structures were investigated by photoluminescence. Figure 6 shows the PL spectra obtained by excitation of a sample containing a structure of 10 periods with

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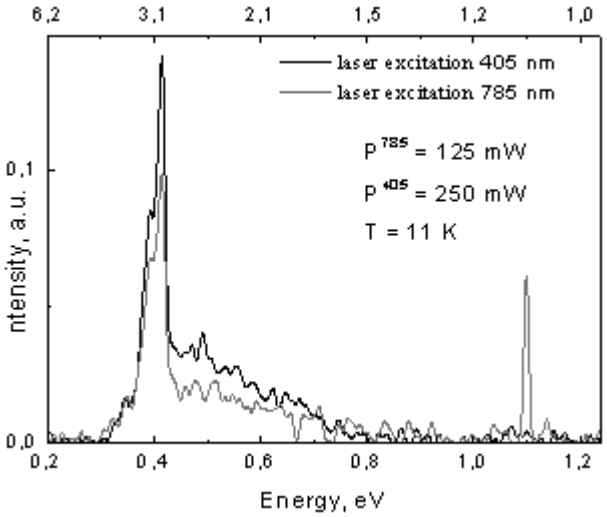


Figure 6. Photoluminescence spectra from samples including a structure with quantum wells $Ge_{0.3}Si_{0.63}Sn_{0.07}$/Si.

a violet laser with an excitation wavelength of 405 nm and an infrared laser with an excitation wavelength of 785 nm. The period of the structure consisted of a layer $Ge_{0.3}Si_{0.63}Sn_{0.07}$ with a thickness of 2 nm and a layer of Si 7 nm thick. In the case of a violet laser, the radiation passes by about 250 nm, which exactly corresponds to the thickness of an epitaxial film grown on a Si substrate and containing a multilayer periodic structure. Therefore, we see a PL signal in the region of 3 microns associated with a multilayer periodic structure, and there is no signal from a silicon substrate in the region of 1.1 microns. An increase in the excitation length to 785 nm leads to an increase in the absorption depth of radiation, radiation penetrates into the substrate. On the PL spectrum, in addition to the signal in the region of 3 microns, a PL signal from silicon appears in the region of 1.1 microns. However, in this case, the intensity of FL in the long-wave infrared region decreases at a maximum of PL at about 3 microns. Decoding the signal in the middle infrared range requires further calculations of the zone structure of the material with GeSiSn layers. Nevertheless, it can be seen that such structures exhibit PL in the infrared range.

Thus, on the basis of multilayer structures with pseudomorphic GeSiSn layers, a technology for the growth of a material demonstrating a PL signal as in the infrared range was developed.

IV. Conclusion

The growth of multilayer structures with GeSiSn quantum wells has been studied and 2D-3D transitions for GeSiSn films with a high tin content of 14 and 18% have been established. The annealed samples were analyzed by X-ray diffractometry and the region of thermally stable compounds was determined. This temperature range ranges from 300–550°C. A photoluminescence signal in the infrared region from a structure with pseudomorphic GeSiSn layers is demonstrated. A material has been obtained that demonstrates a photoluminescence signal in the infrared range.

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