Strained GeSiSn Nanoscale Materials Grown by MBE on Si(100)

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Abstract: - The dependence of the critical thickness transition of two-dimensional growth regime to three-dimensional of temperature and composition of the GeSiSn film on Si(100) was studied. The formation of multilayer structures with pseudomorphous GeSiSn layers without relaxed buffer layers directly on Si have been investigated. A possibility of synthesizing multilayer structures by molecular beam epitaxy was shown, and the crystal lattice constants using the high-resolution transmission electron microscopy were determined. Based on multilayer GeSiSn/Si structures the p-i-n-diodes, which demonstrated the photoresponse increasing by several orders of magnitude compared to the Sn-free structures at an increase in the Sn content, were created. Nanostructures based on GeSiSn layers have demonstrated the photoluminescence at 0.7–0.85 eV.

Key-Words: - Silicon, Germanium, Tin, MBE, Strained layers, Optical properties.

1 Introduction

Nanostructures are extremely important objects for nano- and optoelectronics. The studies in teh field are mainly focused on modifying the materials to improve their optical and electronic properties in order to provide the efficient light emission or absorption [1, 2, 3].

Molecular beam epitaxy (MBE) multilayer Ge-based heterostructures can comprise various strained pseudomorphous layers with the lattice constants conjugated to the silicon substrate. Different morphological states are characteristic of the layers: These may be atomic-smooth wetting layers and 3D islands of different size – from hut-clusters to quantum stretching threads. The strained state of epitaxial layers is varied by adding various materials, for instance, C or Sn, to change the band structure of the material.

For recent years, Ge-Si-Sn-based materials have become of special focus due to their potential applications in integrated silicon photonics, micro- and nanoelectronics, photovoltaics [4-6]. Addition of Sn to Ge makes it possible to control the lattice constant, energy diagram, charge-carriers mobility, efficient mass and defects. Besides, the minimum of the conductivity band for the L and Γ-valley decreases with an increase in the Sn content, the decrease at the Γ-point becomes faster. As a result, GeSn may behave as a direct band semiconductor at the 10% Sn content in relaxed layers and 6% in the films with stretching deformations [7, 8]. The progress in the field of GeSn, GeSiSn [9-11] layer growth opens the way to modifying the band structure by controlling the voltage and composition. Besides changes in the electron and optical properties, the surface Sn favors the adatom surface diffusion and the appearance of a series of superstructures unobserved in the GeSi [12] system. The main problems in synthesis of epitaxial GeSn and GeSiSn film are the low equilibrium solubility of Sn in Ge and Si (<1%), segregation and precipitation; they are solved using nonequilibrium growth techniques such as MBE, magnetron sputtering, solid phase epitaxy, recrystallization and gas phase epitaxy (GPE) [13]. Ge-Si-Sn-based epitaxial layers containing up to 25% of Sn were obtained by reducing the growth temperature, controlling lattice misfits and the strained state [14]. Structures with thick relaxed Ge, GeSn or GeSiSn layers are reported in most of the contributions on GeSn, GeSiSn growth. The main drawback of these structures is the presence of threading dislocations that worsen structural and optical properties of the material. In the present work, we suggest to use pseudomorphous elastic-strained GeSiSn films grown directly on Si rather than relaxed layers. The principal advantage of pseudomorphous films against thick relaxed layers is that they are free of dislocations and coherent to the substrate. GeSiSn films are more thermostable than GeSn [15], their lattice constants and bandgap widths can be individually controlled as dependent on the composition. We have synthesized strained multilayer structures with pseudomorphous GeSiSn layers that provide increasing photoresponse in the longwave IR region as the Sn concentration increases up to 10 %.

3 Experimental

An MBE installation Katun-C equipped with two electron beam evaporators for Si and Ge was used for synthesis. Sn, B and Sb were evaporated from effusion cells. When triple GeSiSn compounds were grown, germanium also was evaporated from an effusion cell. The base pressure of the MBE system was 1×10^{8} Pa. Ultrahigh vacuum MBE was used for synthesis of the structures containing pseudomorphous GeSiSn layers of different compositions (0 to 10% of Sn) and thicknesses (2 to 3.5 nm). The temperature and growth rates of GeSiSn layers were varied between 100-150 ºC and 0.075-0.43 ML/s (1 Sn ML on Si(100) = 0.184 nm), respectively. GeSiSn layers were grown over Si at 500 ºC. Changes in the surface morphology and structure during GeSiSn and Si film growth were controlled using reflection high energy electron diffraction (RHEED). The electron energy was 20 keV. Analysis of spatial-temporal RHEED intensity distributions allowed us to identify the superstructures and the onset of island formations. The moment of 2D-3D transition was determined from the time dependent RHEED intensity along one of strains where a voluminous reflex appeared. The crystal structure of growing layers was studied using high-resolution transmission electron microscopy (TEM) with an electron microscope JEOL-4000EX (electron energy 400 keV, resolution 0.165 nm). TEM images were processes using digital micrograph software. Imaging and quantitative measurement of the lattice distortions and deformation fields were carried out by the method of geometrical phase [16].

p-i-n-Structures with pseudomorphous GeSiSn layers in the i-region were grown to study electrophysical properties. The structure was grown on a doped n^{+}-Si substrate with 0.01 ohm·cm resistivity. The upper contact layer p+-Si was 300 nm thick with the boron acceptor concentration $p=5\times10^{18}$ cm^{-3}. Round mesa-shaped samples of 3-4 mm in diameter were obtained in vacuum using chemical etching and spraying of aluminum contacts. Vertical photocurrent spectra were acquired with an IR Fourier spectrometer “VERTEX 70” from Bruker. The optical properties of the structures studied by photoluminescence spectroscopy (PL). They used a monochromator ACTON 2300i and cooled OMA-V detector based on line-of InGaAs photodiodes with sensitivity band from 1.1 to 2.2 microns. For photoluminescence excitation laser light used Nd: YAG (532 nm).

4 Results and discussion

Synthesis of multilayer structures comprising elastically strained pseudomorphous GeSiSn layers required dependences of the 2D-3D transition thickness on temperature and compositions of the GeSiSn films to be studied at various lattice misfits. The approach was similar to that used for studying pure germanium growth on Si(100) [17]. A kinetic diagram of GeSiSn growth at 2 % misfit is shown in Fig. 1. Generally, an increase in the critical

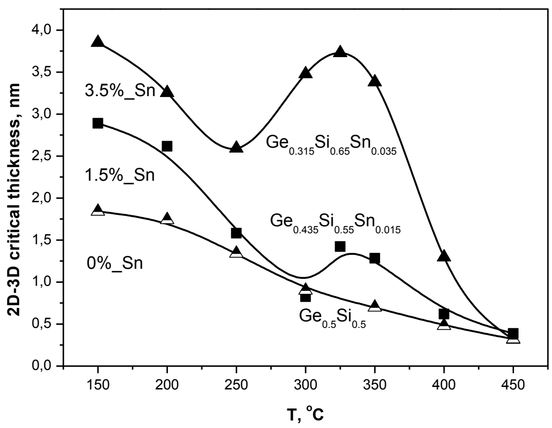

Fig. 1. Temperature dependence of the 2D-3D transition for GeSiSn films with Ge content: 31.5, 43.5 and 50 % for a 2% misfit with Si.

based on the growth diagrams. The GeSiSn growth temperature was chosen to meet the epitaxial growth conditions and to suppress Sn segregation [18]. The optimal temperature of GeSiSn deposition was established to range from 100 to 200 ºC. The pseudomorphous GeSiSn layer was then grown over by a 5-20 nm thick silicon layer at 500 ºC. The thickness of Si was chosen to obtain a smooth surface. A series of superstructures similar to those observed during the growth of pure tin submonolayer [19] was a result of tin segregation on the surface during the growth of Si over GeSiSn. Fig. 2 shows a RHEED pattern with the (4×4)

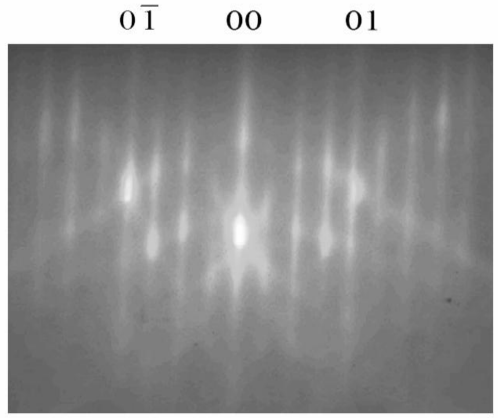

Fig. 2. RHEED pattern along the [110] surface of Si with a superstructure (4 × 4), the coating layer containing GeSiSn c Sn 3.5%

superstructure, which is typical of the Si surface over GeSiSn layers through all the periods of the multilayer GeSiSn/Si heterostructure at the 3 to 10% Sn content and the covering growth temperature of 500 ºC. As the Sn content increases to above 10% at Si growing over GeSiSn, a two-domain superstructure (5×1) becomes observed. The (5×1) superstructure is typically observed at a higher Sn covering on Si(100) [28] and, hence, indicates strengthening of the Sn segregation effect to the surface. Reduction of the temperature of covering growth prevents the segregation phenomenon and smoothens the roughness of the Si film over the GeSiSn layer. TEM was used to characterize the crystal perfection of the heterostructures under study (Fig. 3). Inspection of Fig. 3 leads to conclude that

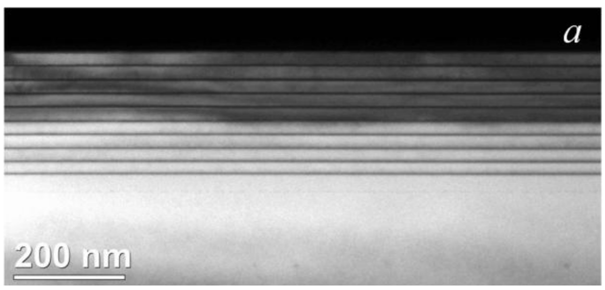

Fig. 3. TEM image of $Ge_{0.5}Si_{0.45}Sn_{0.05}$/Si heterostructure with period 25 nm.

the structures are free of dislocations and crystal-perfect. The crystal lattice distortions and deformation fields were visualized and measured in the TEM images of the multilayer structures GeSiSn/Si using the method of geometric phase. The experimentally measured interplanar distances ($d_{002} = 0.29$ nm, $d_{111} = 0.32$ nm, $d_{220} = 0.192$ nm), with the sample presented in Fig. 6 as an example, are to show that the tetragonal lattice with constants $a = 0.543$ nm and $c = 0.58$ nm is characteristic of GeSiSn layers. We find constant of GeSiSn cubic lattice as equal to 0.562 nm. The lattice constant is 0.5% different from the initial value preset before starting the growth of the multilayer structure. Fig. 4 shows the lattice

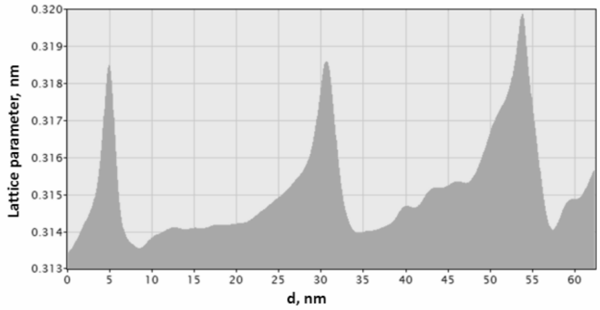

Fig. 4. A profile of the lattice parameter from the film thickness along <111> for the multilayer $Ge_{0.5}Si_{0.45}Sn_{0.05}$/Si heterostructure.

constant profile as a function of film thickness along <111> direction in the multilayer structure with ten periods including $Ge_{0.5}Si_{0.45}Sn_{0.05}$ and Si layers. Irrespective of the peaks observed at 5, 30 and 55 nm depth from the film surface, the constants of the GeSiSn cubic lattice are no more than 0.5 % different.

The change of the lattice constant (Fig. 4) also indicates a gradual decrease in its value during growing over by the silicon layer after the strained GeSiSn layer growth.

The p-i-n-structures shown in Fig. 5 were

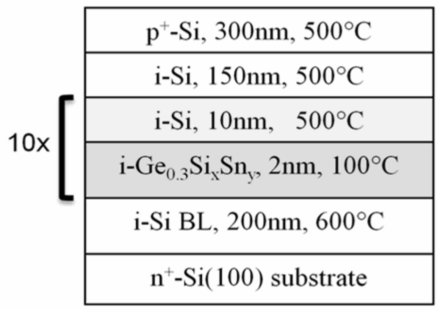

Fig. 5. Scheme of the p-i-n structure.

fabricated to investigate the electrophysical properties of multilayer periodic structures with pseudomorphous GeSiSn layers. The result of photoelectric measurements is presented in Fig. 6.

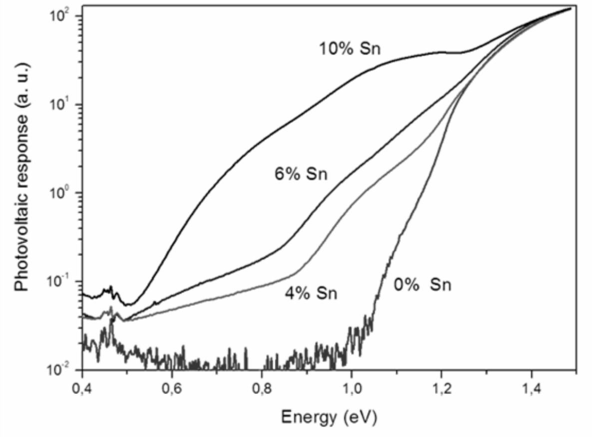

Fig. 6. A series of photoconductivity spectra in the photovoltaic regime at zero bias for the samples with the different Sn content in the p-i-n structure.

The photoconductivity spectra were acquired in the photovoltaic regime at zero shift. An increase in photoresponse with is observed as the Sn concentration in the GeSiSn layer increases from 0 to 10%. The maximal photoresponse is at the 10% Sn content and covers the wavelengths from near- to mid-IR ranges. The photoconductivity increases by 2-3 orders of magnitude compared to the multilayer structures on GeSi quantum wells.

The optical properties of multilayer structures with GeSiSn layers studied using photoluminescence. The PL signal was excited Nd: YAG laser (532 nm), the pump power varied from 20 to 900 mW. Figure 7 shows the

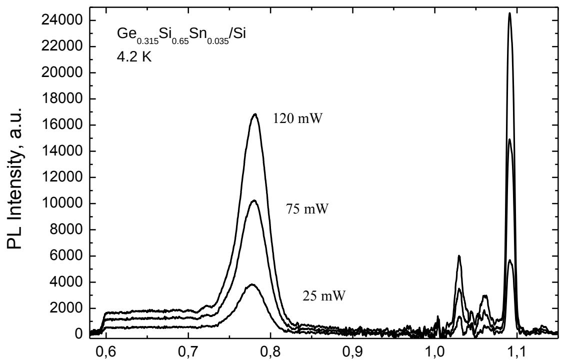

Fig. 7. Photoluminescence spectra obtained at a temperature of 4.2 K for the heterostructure containing 3.5 % Sn.

photoluminescence spectra obtained at a temperature of 4.2 K for the heterostructure containing 3.5 % Sn. Luminescence is observed in the range of 0.7 eV to 0.85‒maximum intensity at a photon energy of 0.77 eV, which corresponds to a wavelength of 1.61 microns. With increasing GeSiSn thickness from 2 to 3 nm, and decreasing temperature from 150 to 100 C luminescence signal is reduced, which may be caused by the growth of defects in the crystal structure. Progress to longer wavelengths greater than 2 microns require an increase in the content of Sn in GeSiSn layers of more than 10 %.

5 Conclusion

Regularities of the formation of multilayer structures on quantum wells comprising pseudomorphous GeSiSn layers without relaxed buffer layers but creating the structures directly on Si were studied for the first time. The obtained TEM data proved the crystal perfection of the samples under study. The multilayer periodic GeSiSn/Si heterostructures demonstrated the photoresponse increasing by several orders of magnitude compared to the Sn-free structures at an increase in the Sn content. Nanostructures based on GeSiSn layers have demonstrated the photoluminescence at 0.7‒0.85 eV.

6 Acknowledgment

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References:

[1] A.I. Yakimov, A.I. Nikiforov, V.A. Timofeev, A.A. Bloshkin, V.V. Kirienko and A.V. Dvurechenskii. Midinfrared photoresponse of Ge quantum dots on a strained $Si_{0.65}Ge_{0.35}$ layer. *Semiconductor Science Technolology,* Vol.26, 2011, pp. 085018-085022.

[2] S. Wirths, et al., Lasing in direct-bandgap GeSn alloy grown on Si. *Nature Photonics*, Vol.9, 2015, pp. 88–92, doi:10.1038/nphoton. 2014.321.

[3] Dainan Zhang et al. “MBE growth of ultra-thin GeSn film with high Sn content and its

infrared/terahertz properties”, *Journal of Alloys and Compounds* , Vol.665, 2016, pp. 131-136.

[4] B. R. Conley, H. Naseem, G. Sun, P. Sharps, Shui-Qing Yu. High efficiency MJ solar cells and TPV using SiGeSn materials. *Photovoltaic Specialists Conference (PVSC)*, vol.38th IEEE, 2012, pp. 001189-001192.

[5] M. Oehme, M. Schmid, M. Kaschel, M. Gollhofer, D. Widmann, E. Kasper, and J. Schulze. GeSn p-i-n detectors integrated on Si with up to 4% Sn. *Applied Physics Letters*, Vol.101 (2012), p. 141110.

[6] S. Wirths, D. Stange, M.-A. Pampillón, A. T. Tiedemann, G. Mussler, A. Fox, U. Breuer, B. Baert, E. San Andrés, N. D. Nguyen, J.-M. Hartmann, Z. Ikonic, S. Mantl, and D. Buca. High-k Gate Stacks on Low Bandgap Tensile Strained Ge and GeSn Alloys for Field-Effect Transistors. *ACS Applied Materials Interfaces*, Vol.7 (2015), p. 62-67.

[7] K. Kostecki, M. Oehme, R. Koerner, D. Widmann, M. Gollhofer, S. Bechler, G. Mussler, D. Buca, E. Kasper, J. Schulze. Virtual Substrate Technology for Ge1-XSnX Heteroepitaxy on Si Substrates. *ECS Transactions*, Vol.64 (2014), p. 811-818.

[8] S. Oguz, W. Paul, T. F. Deutsch, B-Y. Tsaur and D. V. Murphy. Synthesis of metastable, semiconducting Ge-Sn alloys by pulsed UV laser crystallization. *Applied Physics Letters*, Vol.43 (1983), p. 848-850.

[9] J. Xie, A.V.G. Chizmeshya, J. Tolle, V.R. D’Costa, J. Menendez and J. Kouvetakis. Synthesis, Stability Range, and Fundamental Properties of Si− Ge− Sn Semiconductors Grown Directly on Si (100) and Ge (100) Platforms. *Chemistry of Materials*, Vol.22 (2010), p. 3779-3789.

[10] S. Wirths, Z. Ikonic, A.T. Tiedemann, B. Hollander, T. Stoica, G. Mussler, U. Breuer, J.M. Hartmann, A. Benedetti, S. Chiussi, D. Grutzmacher, S. Mantl and D. Buca. Tensely strained GeSn alloys as optical gain media. *Applied Physics Letters*, Vol.103 (2013), pp. 192110(1-5).

[11] V. Mashanov, V. Ulyanov, V. Timofeev, A. Nikiforov, O. Pchelyakov, Ing-Song Yu, Henry Cheng. Formation of Ge-Sn nanodots on Si(100) surfaces by molecular beam epitaxy. *Nanoscale Research Letters*, Vol.6 (2011), pp. 85-90.

[12] A.I. Nikiforov, V.I. Mashanov, V.A. Timofeev, O.P. Pchelyakov, H.-H. Cheng. Reflection high energy electron diffraction studies on $Si_xSn_yGe_{1-x-y}$ on Si(100) molecular beam epitaxial growth. *Thin Solid Films*, Vol.557 (2014), pp. 188-191.

[13] A. Harwit, P. Pukite, J. Angilello, and S. Iyer. Properties of diamond structure SnGe films grown by molecular beam epitaxy. *Thin Solid Films*, Vol.184 (1990), pp. 395-401.

[14] M. Oehme, K. Kostecki, M. Schmid, F. Oliveira, E. Kasper, J. Schulze. Epitaxial growth of strained and unstrained GeSn alloys up to 25 % Sn. *Thin Solid Films*, Vol.557 (2014), pp. 169-172.

[15] J. Xie, J. Tolle, V. D’Costa, A. Chizmeshya, J. Menendez and J. Kouvetakis. Direct integration of active $Ge_{1-x}(Si_4Sn)x$ semiconductors on Si(100). *Applied Physics Letters*, Vol.95 (2009), pp. 181909(1-4).

[16] A. K. Gutakovskii, A. L. Chuvilin, S. A. Song. Application of high-resolution electron microscopy for visualization and quantitative analysis of strain fields in heterostructures. Bulletin of the Russian Academy of Sciences. Physics, Vol.71 (2007), pp. 1426-1432.

[17] A.I. Nikiforov, V.V. Ulyanov, V.A. Timofeev, O.P. Pchelyakov. Wetting layer formation in superlattices with Ge quantum dots on Si(100). *Microelectronics Journal*, 40 (2009) pp. 782-784.

[18] T. Tsukamoto, N. Hirose, A. Kasamatsu, T. Mimura, T. Matsui and Y. Suda. Investigation of Sn surface segregation during GeSn epitaxial growth by Auger electron spectroscopy and energy dispersive x-ray spectroscopy. *Applied Physics Letters*, Vol.106 (2015), pp. 052103(1-4).

[19] K. Ueda and K. Kinoshita, M. Mannami. Study of superstructures on Sn/Si(001) by means of RHEED-LEED-AES. *Surface Science*, Vol.145 (1984), pp. 261-268.