Photoluminescence and infrared spectroscopy studies of thin Ge$_{1-x}$Sn$_x$ heterostructures

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Abstract. Elastically strained metastable GeSn layers with mole fraction of tin up to 0.15 was grown on (001) Si substrates with different misorientation. Photoluminescence spectra (PL) at room temperature and infrared (IR) spectroscopy spectra at helium temperature were measured. The direct edge of intrinsic absorption in the region of 0.71-0.72 eV was observed in grown structures with a tin content of about 12-13%.

1. Introduction

Alloys in the Si–Ge–Sn material system hold promise for fabrication of monolithic optoelectronic systems based entirely on Group-IVA and working in the near- and mid-infrared regions. Previously, direct optical transitions have been demonstrated in momentum space in the photoluminescence spectra up to room temperature [1, 2]. Modulators, light emitting diodes (LEDs), and photodetectors based on Ge$_{1-x}$Sn$_x$ are promising for using in silicon photonics [3-6]. In [7] the possibility of obtaining laser generation in Ge$_{0.88}$Sn$_{0.12}$ layers grown on a silicon wafer with a germanium buffer layer was shown.

With increasing Sn content in a Ge$_{1-x}$Sn$_x$ alloy, the energy of the $\Gamma 7$ conduction-band minimum decreases more rapidly than that of the $L 6$ minimum. Theoretical calculation of band structures of germanium and gray tin ($\alpha$-Sn), which is a semimetal with a band gap of $-0.40$ eV, predicts that an unstrained Ge$_{1-x}$Sn$_x$ alloy should have a direct band gap at a Sn mole fraction $x = 0.6$. However, calculations show [8, 9] that the biaxial-tension strains, including heteroepitaxial ones, also result in a band-gap decrease; the effect of strain on the width of the direct band gap is much stronger. The transition from an indirect to a direct-gap material can be observed at a relatively small tin mole fraction $x = 0.02$. Available experimental data give a value $x \approx 0.09$ for the implementation of this transition [10, 11].

While the material system under discussion obviously holds much promise for both fundamental studies and applications, there are a number of factors hindering the fabrication of experimental samples with high crystalline perfection. At thermodynamic equilibrium, the solubility limit in germanium of $\alpha$-Sn, which has a diamond-like crystal lattice and exists only at temperatures lower than 13.5°C, does not exceed 0.5%, and the solubility limit in silicon is 1.2%. The Sn atom radius (0.158 nm) is larger than that of Si and Ge (0.133 and 0.139 nm, respectively). This, along with a low value of the surface free energy of Sn, leads to Sn segregation during the epitaxial growth. Furthermore, the mismatch of the lattice-constant of $\alpha$-Sn and Ge and Si is 14.7% and 19.7%, respectively, that inevitably leads to problems associated with the formation of defects during the epitaxial growth of GeSn on Si or Ge wafers.
The epitaxial growth of Si–Ge–Sn structures has been conventionally performed by low-temperature (~300–400°C) low-pressure gas-phase epitaxy [12]. Molecular-beam epitaxy (MBE) has also been used for this purpose [13]. The main problem encountered in MBE is the strong tendency toward the surface segregation of tin under ultrahigh-vacuum conditions. For suppression of this effect, the use of even lower growth temperatures (around 150°C) is required. Epitaxy at such low temperatures results in a high density of intrinsic point defects, which adversely affect the photoluminescence efficiency. In this paper, we present structural and optical characterization of MBE grown Ge$_{1-x}$Sn$_x$ for group IV photonic devices.

2. Experimental

Ge$_{1-x}$Sn$_x$ heterostructures were grown on a Ge-buffered Si (100) wafer (Ge-VS) with up to 4° misorientation towards [110]. A set of Ge$_{1-x}$Sn$_x$ structures with Sn concentrations ranging between 0.09 and 0.15 have been grown and covered by a Ge cap-layer [14].

X-ray diffraction (XRD) has been used to study the crystalline quality and the strain relaxation mechanisms in the grown layers. The optical quality and the light emission were investigated by room temperature photoluminescence (PL) and infrared (IR) transmission spectroscopy in a wide temperature range.

Wafer misorientation leads to an improvement of conditions for the incorporation of tin and germanium adatoms into steps with a height of one monolayer which separate the terraces on the growing layer surface and represent drains for adatoms. This is especially important for low-temperature growth when characteristic migration length of adatoms is small. Surface segregation during epitaxial growth also depends on the efficiency of incorporation of tin adatoms into the GeSn crystal lattice.

3. Results and discussion

Recently, in work [14] the results of XRD for the Ge$_{1-x}$Sn$_x$ structures and the description of phase decay of metastable Ge$_{1-x}$Sn$_x$ layers have been demonstrated. Figure 1 shows the XRD rocking curves near the (004) reflection for samples C and D.

![Figure 1. Experimental rocking curves (004) of samples C (a), D (b).](image)

Despite the metastable character of Ge$_{1-x}$Sn$_x$ layers, they maintain huge elastic deformation (>2%) of the lattice without signs of plastic relaxation. The tin mole fraction in the samples with unrelaxed GeSn layers is as large as $x = 0.153$. The main parameters of the grown layers are summarized in Table 1.
Table 1. Parameters of the Ge$_{1-x}$Sn$_x$ structures grown by MBE

| Number | Substrate | Orientation | $T_{Sn}, ^\circ C$ | Sn concentration, % | Total thickness, nm | Ge cap-layer, nm |
|--------|-----------|-------------|-------------------|---------------------|-------------------|-----------------|
| A      | Si (001)  | 4° to (110) | 980               | 9.5                 | 17.8              | –               |
| B      | Si (001)  | 0.5°        | 980               | 9.7                 | 18.8              | 5               |
| C      | Si (001)  | 0.5°        | 1000              | 12.8                | 18                | 14              |
| D      | Si (001)  | 4° to (110) | 1000              | 15.3%               | 16                | 4               |

It is worthwhile to say that, according to the calculations [15], Ge$_{1-x}$Sn$_x$ solid alloys under large compressive strain are indirect-gap semiconductors. The transition to the direct-gap semiconductors is expected at compressive strain of about -1.05%. The remarkable property of Ge$_{1-x}$Sn$_x$ grown on Ge-VS is that solid alloys with the direct and indirect fundamental absorption edges can be obtained by changing the built-in strain.

In some theoretical works [16, 17], it was shown that for relaxed Ge$_{1-x}$Sn$_x$ solid alloys with a tin content $x$ over 0.06, the bottom of the conduction band is the G-point of the Brillouin zone. As the valence band top, regardless of the composition, is also at the G-point, relaxed Ge$_{1-x}$Sn$_x$ with $x > 6\%$ should be a semiconductor with a direct edge of intrinsic absorption.

For strained Ge$_{1-x}$Sn$_x$ epitaxial layers grown on Ge-VS, the difference between a local minimum at the G point and lowest local minima at the L-points is further increased due to compressive strain. Therefore, the transition to the direct self-absorption edge for strained Ge$_{1-x}$Sn$_x$ epitaxial layers is achieved at $x = 10\%$. Despite the indirect absorption edge in Ge$_{1-x}$Sn$_x$ solid alloys with $x$ of about 4% or more, it is possible to observe phononless luminescence that is caused by the recombination of electrons from the G-point with holes also located near the G-point. The emergence of electrons in the neighborhood of a local minimum in the G-point is due to the thermal filling of the respective states. Therefore, photoluminescence (PL) measuring at relatively high temperatures (around room temperature) is crucial to determine the spectral position of the direct self-absorption edge. The IR transmission spectra was also used to evaluate the spectral position of the direct self-absorption edge.

![Figure 2. PL spectra at room temperature for structures D, A and C.](image)

PL spectra were measured at 300K at excitation power density on the sample of about 5 W/cm$^2$. The radiation was registered by the method of synchronous detection with using a suitably selected cooled InGaAs diode (with the red edge of the sensitivity at a wavelength of 2.4 µm), equipped with a low-noise preamplifier with a cooled load. An asymmetrical PL peak with a maximum at 0.715 eV for...
film C was registered (figure 2). The FWHM band (40 meV) was of the order of the thermal energy at room temperature. Thus, this band has the characteristic features of radiation of low-density electron-hole plasma at a temperature of about 300 K. The spectral position of the band maximum is significantly above the indirect absorption edge of Ge (0.66 eV) and significantly lower than the direct self-absorption edge of GeSn (0.75 eV). Thus, the peak near 0.715 eV should be attributed to the radiation from a GeSn layer, which corresponds to the recombination of electrons and holes located near the G point.

Figure 3. IR transmission spectrum of structure D at 5 K.

IR transmission spectra at helium temperature were measured to confirm the interpretation of the emission line. Figure 3 shows IR transmission spectrum for structure D at 5 K. This structure is characterized by a higher tin content, and has a smaller thickness, which is important to look for features associated with the direct edge. The spectrum distinctly shows a valley at about 0.79 eV. This value is significantly above the indirect self-absorption edge of Ge and considerably lower than the direct self-absorption edge of Ge at 5 K. Therefore, the valley around 0.79 eV can be associated with the direct self-absorption edge in the GeSn layer.

4. Conclusion
In conclusion, taking into account the temperature dependence of the GeSn band gap and the fact that the concentration of tin is larger in structure D compared to C, the IR transmission spectrum in figure 3 confirms our suggestion. As a matter of record, it is suggested that at room temperature the investigated structures with a tin content of about 12-13% have the direct self-absorption edge located in the region of 0.71-0.72 eV. This value corresponds to a tin concentration of about 5% in the Ge_{1-x}Sn_x layer with a greater thickness, according to available literature data. This contradiction can be explained by the fact that the tin concentration is affected by the GeSn layer imperfection and the magnitude of the strain. Obviously, these characteristics may be radically different for thick (90 nm) GeSn layers [6].

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References
[1] R Ragan, H A Atwater 2000 *Appl. Phys. Lett.* 77 3418
[2] G Grzybowski, R T Beeler, L Jiang, D J Smith, J Kouvetakis, J Menendez 2012 *Appl. Phys. Lett.* 101 072105
[3] B R Conley, A Mosleh, S A Ghetmiri, W Du, R A Soref, G Sun, J Margetis, J Tolle, H A Naseem and S-Q Yu 2014 *Opt. Express* 22 15639
[4] M Oehme, J Werner, M Gollhofer, M Schmid, M Kaschel, E Kasper and J Schulze 2011 *IEEE Photonics Technol. Lett.* 23 1751
[5] E Kasper, M Kittler, M Oehme and T Arguirov 2013 *Photonics Res.* **1** 69
[6] W Du, Y Zhou, S A Ghetmiri, A Mosleh, B R Conley, A Nazzal, R A Soref, G Sun, J Tolle, J Margetis, H A Naseem and S-Q Yu 2014 *Appl. Phys. Lett.* **104** 241110
[7] S Wirthst, 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 2015 *Nature photonics* **9** 88
[8] R A Sofer, L Friedman 1993 *Superlattices and Microstructures* **14** 189
[9] O Gurdal, P Desjardins, J R A Carlsson, N Taylor, H H Radamson, J-E Sundgren, J E Greene 1998 *Appl. Phys.** **83** 162
[10] G He, H A Atwater 1997 *Phys. Rev. Lett.* **79** 1937
[11] J Mathews, R T Beeler, J Tolle, C Xu, R Roucka, J Kouvetakis, J Menéndez 2010 *Appl. Phys. Lett.* **97** 221912
[12] M R Bauer, C S Cook, P Aella, J Tolle, J Kouvetakis, P A Crozier, A V G Chizmeshya, D J Smith, S Zollner 2003 *Appl. Phys. Lett.* **83** 3489
[13] H Lin, R Chen, W Lu, Y Huo, T I Kamins, J S Harris 2012 *Appl. Phys. Lett.* **100** 102109
[14] Yu G Sadofyev, V P Martovitsky, A V Klekovkin, V V Saraykin, I S Vasil’evskii 2015 *Semiconductors* **49** 1564
[15] D Stange, S Wirths, N von den Driesch, G Mussler, T Stoica, Z Ikonic, J M Hartmann, S Mantl, D Grützmacher and D Buca 2015 *ACS Photonics* **2** 124
[16] V R D’Costa, Y-Y Fang, J Tolle, J Kouvetakis and J Menéndez 2010 *Thin Solid Films* **518** 2531
[17] N Bhargava, J P Gupta, T Adam and J Kolodzey 2014 *J. Electron. Mater.* **43** 931