Structure and surface morphology of GeSn/Si(001) layers grown by HW CVD with co-evaporation of Sn

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Abstract. This paper presents the results of the investigation of Ge_{1-x}Sn_x epitaxial layers grown by the hot wire chemical vapor deposition (HW CVD) method with simultaneous evaporation of Sn from a standard effusion cell. The Ge_{1-x}Sn_x with a Sn molar fraction of 7.2% and a full width at half maximum (FWHM) of the rocking curve of 7.6` demonstrated intense photoluminescence at room temperature. The peaks in the energy bands 0.70 – 0.73 eV and 0.63 – 0.65 eV have been observed in the photoluminescence spectra. These peaks were related to the direct and indirect interband radiative optical transitions in GeSn, respectively.

1. Introduction
Increasing the data transfer rate while reducing power consumption is a key problem in the design of integrated circuits (ICs) based on traditional silicon technology. An alternative approach is to use optical interconnects, which consume less power and provide higher data transfer rates. However, the indirect bandgap of Si is the main problem in the implementation of this approach. Therefore, there is an extensive search for efficient Si-based light emitting sources (for example, Si:Er [1], GeSi/Si nanoislands [2], etc.) and/or other Si-compatible materials (for example, III-V compound semiconductor structures grown on SiGe or Ge buffer layers [3]).

The use of the Ge_{1-x}Sn_x alloy as a material of active layers in light emitting and laser diodes is one of the research directions that has been intensively developing in recent years [4]. At a Sn molar fraction x > 7%, the alloy becomes direct gap [5]. The first GeSn-based laser with optical pumping was demonstrated in 2015 [6]. It is worth noting that the efficiency of photonic devices based on GeSn/Si(001) heterostructures essentially depends on the quality of epitaxial layers.

Low equilibrium solubility of Sn in solid Ge ( < 1 % at.) as well as the high lattice mismatch ( ≈ 15%) between α-Sn and Ge (with lattice constants of ≈ 0.6489 nm and ≈ 0.5664 nm, respectively) are the main factors limiting the growth of high-quality GeSn/Si(001) heterostructures. This alloy was grown mainly by standard molecular beam epitaxy (MBE) with the evaporation of Ge and Sn from effusion cells [7–9] and by chemical vapor deposition (CVD) from GeH₄, Ge₂H₆, etc. and SnD₄ and SnCl₄ used as precursors of Ge and Sn, respectively [10–12]. However, in order to ensure a sufficiently high Sn content, lower substrate temperatures T_s < 300 °C are required, as compared to ordinary epitaxy of Ge. In addition, the epitaxial growth of thick (> 200 nm) GeSn layers with a sufficiently high Sn content (over 10 %) was considered impossible for a long time due to the low growth rates at these temperatures: as a rule the epitaxial growth is disrupted [13]. To date, there have
been several reports on growing such layers. For example, it was reported that GeSn layers with a high Sn content (up to 14%) were grown up to 1 µm thick [14].

On the other hand, in order to grow high-quality Ge epitaxial layers on a Si(001) substrate, we applied low temperature ($T_s \approx 325$ °C) hot wire CVD (HW CVD) [15]. In addition, we have developed a method for growing epitaxial layers of GeSn alloy on Si(001) substrates, which combined HW CVD of Ge and co-evaporation of Sn from an effusion cell. In the present paper, we report the results of investigations of the crystal structure, surface morphology, and photoluminescence of Ge$_{1-x}$Sn$_x$/Si(001) heterostructures first grown by this method.

2. Experimental details
The GeSn/Si(001) heterostructures were grown in an ultra-high vacuum growth setup, close to the one reported in [15], at low substrate temperatures (250 – 325 °C). Single crystal Si(001) substrates with a specific resistivity of $\rho = 12$ Ω·cm were used. A flow of Ge atoms was formed by letting monogermane (GeH$_4$) into the growth chamber, in which it cracked pyrolytically on the surface of a Ta strip (playing the role of a hot wire) heated up to $T_{Ta} = 1200 – 1500$ °C. The Sn flow was formed by evaporation from a standard effusion cell. The growth parameters for obtaining defect-free epitaxial layers of pure Ge on Si(001) substrates by HW CVD [15] ($T_s = 325$ °C and $T_{Ta} = 1400$ °C, pressure of GeH$_4 = 6 \cdot 10^{-4}$ Torr) were selected as the starting ones for growing GeSn layers.

The crystal quality and composition of the GeSn epitaxial layers were examined by X-ray diffraction using a Bruker® D8 Discover™ diffractometer. The surface morphology of the GeSn epitaxial layers was examined by atomic force microscopy using an NT-MDT® Integrator™ instrument. The photoluminescence (PL) spectra of the GeSn/Si(001) epitaxial layers were measured at room temperature in the emission wavelength band from 1.0 µm up to 2.1 µm using a Hamamatsu® G12182-110K InGaAs photodiode. A semiconductor laser diode with an emission wavelength of 445 nm and an output power of $\approx 250$ mW was used as a pumping source.

3. Results and discussion
First, the value of the effusion cell temperature $T_{Sn}$ was determined, at which the GeSn alloy starts growing on the Si(001) substrate. The growth of GeSn alloy layers began in a lower temperature range. At relatively low values of $T_{Sn}$ (870 – 950 °C), the Sn molar fraction $x$ in the GeSn alloy was $< 1\%$ (figure 1) and increased with increasing $T_{Sn}$. At the same time, the crystal quality of the GeSn layers worsened with increasing $T_{Sn}$: the full width at half maximum (FWHM) of the rocking curves measured around the (004) reflection increased from 7.6’ up to 12.0’ (figure 2). The highest concentration of Sn in the GeSn layers (up to 9.8%) was obtained at $T_{Sn} = 1080$ °C. At that, the crystal quality of the layers remained satisfactory: the FWHM of the rocking curve was 11.0’ – 12.0’. On the other hand, at higher values of $T_{Sn}$ (1100 °C) $x$ decreased down to 8.3%, likely due to the surface segregation of Sn.

The surface morphology of the GeSn epitaxial layers essentially depended on the Sn flux onto the substrate. At a low Sn flux ($T_{Sn} \leq 925$ °C), the root mean square roughness (RMS) of the GeSn layer surface was close to the one of pure Ge layers: RMS$_{GeSn} \sim 1.54$ nm whereas RMS$_{Ge} \sim 0.39$ nm. With increasing Sn flux due to increasing $T_{Sn}$, the surface morphology became coarser: at $T_{Sn} = 950$ °C RMS $< 2.5$ nm, at $T_{Sn} = 1040$ °C RMS was $8$–$10$ nm.

The temperature of the Ta stripe, at which the cracking of monogermane takes place, determines the flux of Ge atoms onto the substrate. Figure 3 presents the dependencies of the FWHM of the rocking curves measured in GeSn layers at $T_{Ta}$ for two values of $T_{Sn}$ (900 and 1040 °C). It can be seen that the FWHM decreased monotonically with increasing $T_{Ta}$, i.e. the crystal quality of the GeSn layers improved with increasing $T_{Ta}$. This effect can probably be related to an increase in the ratio of Ge and Sn fluxes and, as a result, to a decrease in the Sn content in GeSn layers.
Figure 1. The dependence of the Sn molar fraction \( x \) in the Ge\(_{1-x}\)Sn\(_x\) layers on the temperature of the effusion cell \( T_{Sn} \).

Figure 2. The dependence of the FWHM of the rocking curves measured in the GeSn layers near the (004) reflection on the temperature of the effusion cell \( T_{Sn} \).

The substrate temperature \( T_s \) essentially affected the incorporation of Sn into the growing layer. The molar fraction of Sn in the GeSn layers \( x \) increased monotonically with decreasing substrate temperature (figure 4). Currently, a further decrease in the substrate temperature (for example, down to 200 °C) is one of the ways of increasing the Sn fraction in GeSn layers.

To investigate the PL spectra of the GeSn layers, they were grown on Ge buffer layers on Si(001) substrates. The technological parameters of the growth of GeSn/Ge/Si(001) structures and some of their structural parameters are presented in table 1.

Figure 5 presents the PL spectra (300 K) of the Ge\(_{1-x}\)Sn\(_x\)/Ge/Si(001) epitaxial heterostructures grown in different conditions. In the PL spectra of samples 11-813 and 11-814, the PL lines were observed with maxima around \( h\nu_m = 0.72 \text{–} 0.73 \text{ eV} \) and \( 0.63 \text{–} 0.65 \text{ eV} \). These PL peaks were related to direct and indirect interband radiative optical transitions, respectively, in GeSn epitaxial layers.
Table 1. Growth process and structure parameters of the GeSn/Ge/Si(001) layers. \( T_{Sn} = 1040 \, ^\circ C \).

| Sample № | Growth parameters | FWHM | \( x, \% \) |
|----------|-------------------|------|-------------|
|          | \( T_s, ^\circ C \) | \( T_{Ta}, ^\circ C \) | GeSn(003), \( ^\circ \) |         |
| 11-813   | 250               | 1450 | 10.02       | 6.51    |
| 11-814   | --/--             | 1500 | 9.71        | 7.24    |
| 11-815   | 300               | --/--| 7.2         | 6.48    |

Figure 5. The PL spectra (300 K) of the \( \text{Ge}_{1-x}\text{Sn}_x/\text{Ge}/\text{Si}(001) \) epitaxial layer grown in different conditions.

4. Conclusions
Finally, the first experiments on growing \( \text{Ge}_{1-x}\text{Sn}_x \) epitaxial layers by HW CVD with evaporation of Sn from an effusion cell have demonstrated this approach to be promising. To date, using this method, \( \text{Ge}_{1-x}\text{Sn}_x \) epitaxial layers have been grown with high crystal quality and a thickness of up to 1 \( \mu \)m with \( x \) up to \( \sim 10 \% \). In the future, in order to increase the Sn fraction in the \( \text{Ge}_{1-x}\text{Sn}_x \) layers, it is planned to carry out the growth experiments at reduced substrate temperatures (by varying the Ge and Sn fluxes). The \( \text{Ge}_{1-x}\text{Sn}_x \) with a Sn molar fraction of 7.2\% and the FWHM of the rocking curve of 7.6\` demonstrated intense photoluminescence at room temperature. The peaks in the energy bands 0.70 – 0.73 eV and 0.63 – 0.65 eV were observed in the PL spectra. These peaks were related to the direct and indirect interband radiative optical transitions in GeSn, respectively.

Acknowledgments
The work has been supported by the Russian Science Foundation (18-72-10061).

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