Conference of Physics of Nonequilibrium Atomic Systems and Composites, PNASC 2015, 18-20 February 2015 and the Conference of Heterostructures for microwave, power and optoelectronics: physics, technology and devices (Heterostructures), 19 February 2015

Thermal stability of Ge/GeSn nanostructures grown by MBE on (001) Si/Ge virtual wafers

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Abstract

A stack of five metastable 200-nm-thick elastically strained GeSn epitaxial layers separated by 20-nm-thick Ge spacers was grown on (001) Si/Ge virtual substrate by MBE. The molar fraction of Sn in different layers varied from 0.005 to 0.10, increasing with the layer distance from the Ge buffer. The phase separation of the GeSn alloy during postgrowth annealing takes place along with plastic relaxation. The phase separation begins well before the completion of the plastic relaxation process. The degree of phase separation at a given annealing temperature depends strongly on the Sn content in the GeSn alloy. The Sn released from the decomposed GeSn alloy predominantly accumulates as an amorphous layer on the surface of the sample.

Keywords: GeSn alloy, direct band gap, metastable alloy, annealing, plastic relaxation, phase separation;

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1. Introduction

Ge$_{1-x}$Sn$_x$ alloys hold promise as direct-gap materials in the family of elementary semiconductors with the diamond lattice. In recent years, there has been a number of studies in which optical transitions direct in reciprocal space were observed in the photoluminescence spectra of these alloys up to room temperature Ragan and Atwater (2000), Grzybowski et al. (2012). In Wirthst et al. (2015), the possibility of attaining laser oscillation in Ge$_{0.88}$Sn$_{0.12}$ layers grown on a silicon wafer with a germanium buffer was demonstrated. Coherent radiation was obtained under optical pumping with a power density of about 400 kW/cm$^2$ at temperatures up to 90 K. Although this result is certainly noteworthy in the scientific context, its importance in terms of applications is not as obvious yet.

Grey tin ($\alpha$-Sn) is a semimetal with the overlap between the conduction and valence bands estimated at 0.4 eV. A simple interpolation between the band structures of germanium and grey tin suggests that unstrained Ge$_{1-x}$Sn$_x$ alloy should have a direct-gap band structure for Sn molar fractions in the range of ~0.2–0.65. In this range of compositions, the band gap $E_g$ of the alloy should vary from 0.55 eV to zero Oguz et al. (1983). Calculations indicate that tensile biaxial strain in Ge$_{1-x}$Sn$_x$ layers, in particular, that appearing upon heteroepitaxy, also leads to a decrease in the band gap, with the effect of strain on the direct gap being much more pronounced than on indirect Sofer and Friedman (1993), Gurdal et al. (1998). The crossover from an indirect- to a direct-gap material may take place for a relatively small Sn molar fraction of $x = 0.02$. The available experimental data indicate that this crossover occurs for $x \sim 0.09$ He and Atwater (1997), Mathews et al. (2010).

However, at thermodynamic equilibrium, the solubility limit of $\alpha$-Sn in germanium does not exceed $x = 0.005$. The atomic radius of Sn (0.158 nm) is larger than that of Ge (0.139 nm).

This, along with a low value of the surface free energy of Sn, leads to a trend towards the segregation of Sn during the epitaxial growth of alloys in the GeSn material system. Furthermore, the large lattice-constant mismatch between $\alpha$-Sn and both Ge and Si (14.7% and 19.7%, respectively) leads to problems associated with the formation of defects during the heteroepitaxy of GeSn on Si or Ge wafers. For these reasons, GeSn alloys with Sn molar fractions in the range of practical interest can be obtained only under conditions far from thermodynamic equilibrium. The grown layers will inevitably be metastable and exhibit a trend to phase separation under external perturbations. In addition, upon the heteroepitaxy of GeSn layers on alien substrates, there appear built-in strains, which modify the band gap and may affect the processes of plastic relaxation and phase breakdown of the alloy.

2. Experimental

The GeSn layers were grown in a Katun MBE system equipped with two electron-beam evaporators for silicon and germanium and two molecular sources of the Knudsen-cell type. The latter ones were used for the co-evaporation of antimony as a surfactant upon the growth of 1-μm-thick Ge buffer layers Sadofyev et al. (2014) and for the evaporation of tin upon the growth of GeSn layers. A built-in reflection high-energy electron diffractometer (RHEED) enabled in situ control of all stages of the growth process. The evaporation rates of Si and Ge were periodically measured using a quartz resonator built into the growth chamber.

The properties of the grown layers were characterized by X-ray diffractometry (XRD) using a PANalytical X’pert Pro Extended MRD diffractometer, secondary-ion mass spectrometry (SIMS) using a CAMECA IMS-4f microprobe mass spectrometer, atomic-force microscopy (AFM) using an NT–MDT Solver P47H unit, and Auger spectroscopy using a O9IOS Auger spectrometer. The annealing of the grown samples was performed in a Modular RTA system in a highly purified nitrogen atmosphere.

Previously, we demonstrated that relatively thick (~0.5 μm) GeSn layers with Sn molar fractions up to 0.075 grown on silicon wafers with a relaxed Ge buffer layer playing the role of a virtual substrate exhibited no signs of plastic relaxation during growth. However, even short-term annealing of such structures caused both plastic relaxation and the release of tin on the surface Sadofyev et al. (2015). The minimum annealing temperature required to initiate these processes depended on the Sn molar fraction in the GeSn layers.

Here, in order to clarify the character of the processes in question, we have grown a multilayer Ge/GeSn structure (sample S050). On top of a 1-μm-thick relaxed Ge buffer deposited on a (001)-oriented silicon wafer, five GeSn layers with nominal thicknesses of 200 nm separated by 20-nm-thick Ge spacers were grown. The molar fraction of Sn was increased with increasing distance of the layers from the buffer. For this purpose, upon the growth of each

consecutive layer, the temperature of the Sn molecular cell was increased in the range of 920–1000°C in steps of 20°C. In the following discussion, the GeSn layers (GeSn1–GeSn3) are numbered in order of increasing distance from the buffer. The growth rate of the GeSn epitaxial layers was maintained at ~3 nm/min. The structure was capped by a 20-nm Ge layer. The growth temperature was close to 150°C. According to the observed RHEED patterns, even at such a low temperature, all grown GeSn layers have single-crystal structure. As the molar fraction of Sn increases, there appear signs of faceting at the surface of the growing layer, which disappear upon the deposition of the Ge spacers. According to the AFM data, the rms surface roughness corresponding to the layer with the highest Sn content grown in these experiments was about 2–3 nm, while the surface roughness of the Ge buffer layer was about 0.7 nm Sadofyev et al. (2014).

The x-ray measurements were carried out using a primary monochromator consisting of a combination of an x-ray mirror and a 4×Ge(220) four-crystal monochromator with a divergence of 12° and a third crystal analyzer 3×Ge(220). The lattice constants of the layers in the direction perpendicular to the growth surface and within the growth plane (a⊥ and a||, respectively) were determined using the (004) and (224) reflections, respectively.

3. Results and discussion

Figure 1 shows a fragment of the two-dimensional reciprocal-lattice region near the (004) reflection for the Si substrate, the Ge buffer layer, and the three GeSn layers with the lowest Sn content (GeSn1–GeSn3). The position of each peak along the Qy axis in the reciprocal space is determined by the Bragg diffraction angle θB Herres et al. (1996):

\[ Q_y = \sin \theta_B \times \cos (\theta_B - \omega) \times 10^4 \]

where ω is the angle of incidence of the x-ray beam on the sample, whose value for the symmetric (004) reflection is close to the Bragg angle. For Si and Ge, \( Q_y = 5674 \) reciprocal lattice units (r.l.u.) and 5455 r.l.u., respectively. The large lattice-constant mismatch between the buffer layer and the substrate (4.18%), leads to complete plastic relaxation of the misfit strain in the buffer layer and to the broadening of the buffer peak along the horizontal axis.

![Fig. 1. Fragment of the two-dimensional reciprocal-lattice region near the (004) reflection for sample S050 including the peaks corresponding to the Si substrate (top), the Ge buffer layer at \( Q_y = 5455 \) r.l.u., and the three GeSn layers closest to the buffer. The peak corresponding to the layer GeSn1 with the lowest Sn content (\( T_{Sn} = 920°C \)) can barely be distinguished from the Ge peak. The peaks from the next two layers GeSn2 and GeSn3 (\( T_{Sn} = 940 \) and 960°C) are clearly visible in the lowest part of the plot.](image)

The position of the peak (or its broadening) along the Qy axis represents the misorientation of the crystallographic planes from (001) Mathews et al. (2010):

\[ Q_y = \sin \theta_B \times \sin (\theta_B - \omega) \times 10^4 \]

The center of the Si peak is located at \( Q_y = -11.2 \) r.l.u.; the corresponding angle of incidence \( \omega = 34.642 \) exceeds the Bragg angle \( \theta_B = 34.564° \) by 0.078°. The broadening of the Ge (004)-reflection peak is \( \Delta(Q_y) = \pm 12.5 \) r.l.u., which corresponds to the
misorientation of the Ge crystal planes by $\Delta \alpha = \pm 0.085^\circ$ with respect to the (001) plane of Si. All of the GeSn layers inherit this misorientation; thus, both the Ge buffer layer and the GeSn layers grown on top of it actually represent a texture owing to the high density of dislocations with a trend to the formation of small-angle boundaries. Note also the enhanced diffuse scattering in the vicinity of the Ge and GeSn peaks.

For such textured samples, a conventional rocking curve recorded with a wide entrance slit at the detector does not provide the sufficient resolution of the peaks corresponding to the GeSn epitaxial layers. Thus, we plot in Fig. 1 on a quadratic scale the $(20-\omega)$ scanning curves for the (004) reflection using the third analyzer crystal. Curves 1 and 2 were recorded immediately after the growth and after a 2-min annealing of the sample at $400^\circ$C, respectively. The Si peak is removed from Fig. 2 because of its high intensity, although it actually was recorded to check the proper adjustment of the diffractometer. From the positions of the maxima in these curves, one can determine the values of $a_\perp$ for the Ge buffer layer and all of the five GeSn layers. In curve 1, there is a series of satellites between the peak of the Ge buffer layer, which is the most intense one, and the next well-resolved peak, corresponding to the GeSn$_2$ layer. The thickness of the latter can be determined from the angular spacing between the satellites. Because of the low Sn content in the GeSn$_1$ layer, the corresponding peak cannot be resolved from the peak of the Ge buffer layer. Thus, the lattice constant in this layer was determined from the fit of the calculated rocking curve to the experimental one. Taking into account the complicated design of the structure as a whole, this may result in a noticeable error in determining the molar fraction of Sn in this layer from the XRD data.

There are three major differences between curves 1 and 2 (Fig. 2), recorded before and after sample annealing, respectively: (i) the total disappearance upon the annealing of the peak from layer GeSn$_5$, grown at the highest temperature of the Sn source used in this study ($T_{Sn} = 1000^\circ$C); (ii) the shift of three other peaks, originating from layers GeSn$_4$–GeSn$_2$, to larger angles, which corresponds to a reduction in the Sn content in these layers; and (iii) better resolution of the peaks from the Ge layer and the GeSn$_1$ layer caused by an increase in the Sn content in the latter.

Thus, the lattice constants $a_\perp$ of the Ge buffer layer and the GeSn layers along the growth direction were determined from the positions of the peaks in Fig. 2. Then, the lattice constants $a_\parallel$ in the growth plane were obtained from the angular values of the third analyzed crystal for each peak position on the asymmetric $(224)$ $(\omega-2\theta)$ scanning curve (Fig. 3). To find the Sn molar fraction in the layers, one needs to determine the relaxed values of the GeSn lattice constants, which can be calculated using the Poisson coefficient $v$, which also depends on the Sn content. Thus, the composition of the layers was determined in two steps, using an approximate value of $v$ for the first iteration and a refined value for the second. For germanium and tin, $v = 0.273$ and 0.300, respectively. The
lattice constant of α-Sn was taken as 6.491 Å.

Fig. 3. ($\omega$–2θ) scanning curves for the (224) reflection recorded (1) immediately after the growth and (2) after a 2-min annealing of the sample at 400°C.

The relaxed lattice constants of the GeSn layers were calculated using the following formula, Chu et al. (1985):

$$\left(\frac{\Delta a}{a_s}\right)_{\text{relax}} = \frac{1 - \nu}{1 + \nu} \left(\frac{\Delta a}{a_s}\right)_{\perp} + \frac{2\nu}{1 + \nu} \left(\frac{\Delta a}{a_s}\right)_{\|}.$$  \hspace{1cm} (1)

For the Ge buffer layer, $a_s$ was taken equal to the lattice constant of silicon; for the GeSn layers, the value of $a_s$ is equal to the lattice constant of the Ge virtual substrate in the growth plane $a_{\text{Ge}}$.

The lattice constant of the Ge layer in the growth plane $a_{\|\text{Ge}} = 5.6650$ Å is greater than that in the perpendicular direction $a_{\perp} = 5.6513$ Å. This results from the fact that the thick Ge layer is fully relaxed at the growth temperature, while, upon cooling to room temperature, it undergoes greater contraction than the substrate since the thermal expansion coefficient of germanium is larger than that of silicon ($\alpha_{\text{Ge,300K}} = 5.7 \times 10^{-6}$, $\alpha_{\text{Si,300K}} = 2.6 \times 10^{-6}$). As the temperature decreases, the mobility of dislocations decreases and the further contraction of the Ge layer occurs only in the perpendicular direction, as described by the Poisson coefficient. Formally speaking, this implies that the relaxation of the Ge buffer layer becomes larger than 100%. According to formula (1), $a_{\text{Ge,relax}} = 5.6572$ Å. The difference $\Delta a = 3.1 \times 10^{-6}$; thus, given the difference between the above values of $a_{\|\text{Ge}}$ and $a_{\text{Ge,relax}}$, one can estimate the temperature of the dislocation "freeze-out" in the 1-μm-thick Ge buffer layer at about 350°C.

In the as-grown sample, the lattice constant of the GeSn layers in the direction perpendicular to the growth surface increases with increasing Sn content in the layers, while their in-plane lattice constant is the same or even somewhat smaller than the lattice constant of the Ge buffer layer. This means that no relaxation of misfit strain takes place during epitaxy and, furthermore, this is indicative of a fairly large concentration of vacancies in the form of some stable complexes, which have compressive effect on the lattice constant. The percentage of plastic relaxation $rel$ for the Ge layer is calculated as $rel_{\text{Ge}} = 100(a_{\text{Ge,relax}} - a_{\text{Si}})/(a_{\text{Ge}} - a_{\text{Si}})$, where $a_{\text{Si}} = 5.43105$ Å. For each GeSn layer, the lattice constant of the previous layer in the growth plane is substituted in place of $a_{\text{Si}}$; e.g., $rel_{\text{GeSn3}} = 100(a_{\text{GeSn3,relax}} - a_{\text{GeSn2}})/(a_{\text{GeSn3}} - a_{\text{GeSn2}})$.

The parameters of the layers determined in the above way are summarized in the table 1.
Table 1. The parameters of the layers.

<table>
<thead>
<tr>
<th>Grown layer</th>
<th>as grown</th>
<th>plastic relaxation, %</th>
<th>after annealing (400°C, 2 min)</th>
<th>plastic relaxation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sn molar fraction</td>
<td></td>
<td>Sn molar fraction</td>
<td></td>
</tr>
<tr>
<td>Ge buffer</td>
<td>~0.005</td>
<td>103.5</td>
<td>0</td>
<td>103.5</td>
</tr>
<tr>
<td>GeSn₁</td>
<td>0.034</td>
<td>-9.9</td>
<td>0.033</td>
<td>69.9</td>
</tr>
<tr>
<td>GeSn₂</td>
<td>0.047</td>
<td>2.7</td>
<td>0.04</td>
<td>0</td>
</tr>
<tr>
<td>GeSn₃</td>
<td>0.072</td>
<td>-1.7</td>
<td>0.066</td>
<td>30.5</td>
</tr>
<tr>
<td>GeSn₄</td>
<td>0.10</td>
<td>-2.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Using the calculated values of the relaxed lattice constants of the GeSn layers of the structure, we can determine the corresponding molar fractions of Sn. They are 0.005, 0.034, 0.047, 0.072, and 0.10 for layers GeSn₁–GeSn₅, respectively. According to the known handbook data for the temperature dependence of the saturated vapor density of tin, in the temperature range used in our experiments, the temperature of the Sn source has to be raised by 110°C in order to increase the Sn vapor density by an order of magnitude. Thus, the variation of the Sn molar fraction by a factor of 20 upon an 80°C increase in the temperature of the Sn molecular cell, which we deduced from the XRD data, is surprisingly large. The expected variation should be no more than a factor of 7. The most abrupt change in the Sn molar fraction (about sevenfold) is observed between layers GeSn₁ and GeSn₂. The Sn molar fraction in layer GeSn₁ (where the Sn content is the lowest, x = 0.005) seems very low for the used growth regimes. Note also that the structural perfection of the layers degrades as the Sn content increases. This is especially pronounced in the layer with the highest molar fraction of Sn (x ~ 0.1) grown in our experiments; the XRD peak of this layer is noticeably broadened (see Fig. 2). A trend to broadening is also observed for the preceding peak, which corresponds to the layer with a Sn molar fraction of x = 0.072.

The profile of the Sn distribution in the as-grown structure determined by SIMS using O₂⁺ primary ions with an energy of 8 keV is shown in Fig. 3, curve 1 for Sn⁺ ions. All five GeSn layers with different Sn content, as well as the thin (20 nm) Ge spacers, are clearly distinguished. Note that, in contrast to the results obtained by XRD, the relative change in the signal from Sn⁺ secondary ions between the neighboring GeSn layers is almost the same for all five of them. The discrepancy between the results obtained by XRD and SIMS for the layers with the smallest molar faction of Sn may be caused by the difference between the physical mechanisms underlying these two methods. In the former, the Sn molar fraction is determined from the deviation of the GeSn lattice constant from that of Ge. I.e., XRD is sensitive to those Sn atoms that are incorporated in the crystal lattice of the GeSn alloy and, thus, contribute to the increase in the lattice volume with respect to Ge. The latter method is sensitive to the total content of Sn in the layer, including atoms in interstitial positions or atoms forming defect–precipitate complexes in the alloy. In particular, there is a well-known effect of impurity gettering by dislocations Ravi (1981). In our case, upon the growth of GeSn on a 1-µm-thick relaxed Ge buffer layer, the density of threading dislocations cannot be lower than 1×10⁶ cm⁻². This creates conditions for the formation of dislocation–precipitate complexes, and, as a result, only a part of Sn introduced into the layer is incorporated into the GeSn crystal lattice in dislocation-free regions. The capacity of this drain channel for Sn atoms is limited by the dislocation density. Thus, the effect of the formation of dislocation–precipitate complexes manifests itself most pronouncedly in XRD measurements for layers grown under low Sn flux densities, comparable to the capacity of the dislocation-related drain channel for Sn atoms. We believe that this factor is responsible for the discrepancy between the XRD and SIMS results for the Sn content in the layers with the smallest Sn molar fractions (layers GeSn₁ and GeSn₂).

The structural parameters of the layers change in a most dramatic way upon annealing (see curves 2 in Figs. 2 and 3 and the table). Apart from the complete disappearance of the peak from layer GeSn₅, with the highest Sn content prior to the annealing, we observe a reduction of the Sn content in layers GeSn₄ and GeSn₃. The effect of the annealing on the layers with lower molar fractions of Sn (layers GeSn₂ and GeSn₁) is less prominent.

The SIMS profiles (see Fig. 4, curve 2) provide more detailed information on the redistribution of Sn in the structure upon annealing. Heat treatment has the least pronounced effect on layers GeSn₁ and GeSn₂, in which the molar fractions of Sn are the smallest. However, the diffusion-related broadening of the Sn distribution profile is still observed for these layers; this broadening leads to a noticeable decrease in the composition modulation depth upon the transition from GeSn layers to Ge spacers. Layers in which the Sn molar fraction was originally equal to or
exceeded 0.046 become significantly depleted of Sn, which, owing to phase decomposition and subsequent diffusion, escape to the surface of the structure. According to the AFM data, this process leads to the noticeable roughening of the surface microrelief. The strength of this effect depends on the amount of Sn in the structure (i.e., on the molar fraction of Sn in the GeSn layers and their thickness); the rms surface roughness of a structure containing 0.5-μm-thick GeSn layers with a Sn molar fraction of 0.075 may change upon annealing from 2 to 40 nm He and Atwater (1997). It is noteworthy that sample annealing does not result in the complete disappearance of the Ge spacers between the GeSn layers. This means that the diffusion of Sn proceeds mainly along the grain boundaries that form in the Ge virtual substrate and thread into the GeSn layers. A certain increase in the Sn content in layer GeSn1 indicates that this diffusion goes in the opposite direction as well.

The presented data give evidence that, with an increase in the molar fraction of Sn in GeSn alloys, their susceptibility to phase breakup accompanied by the layer depletion of Sn increases. The annealing of GeSn layers causes two competing processes, i.e., the phase decomposition of the alloy with the subsequent escape of Sn to the surface, mainly along the grain boundaries, and the plastic relaxation of the alloy without changes in the composition. The dominance of either process is determined by the difference in the Sn content between the adjacent layers. Phase decomposition starts up well before the plastic relaxation of elastically strained epitaxial GeSn layers is completed, and the relaxation itself has little influence on the alloy breakup and the diffusion of Sn. We believe that this is related to the increased concentration of defects in GeSn layers grown on a Ge virtual substrate.

The work was supported by Russian Science Foundation, grant No. 14-22-00273.

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