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Research Article

Optimal Regime for Growth of Epitaxial Germanium Layers from the Liquid Phase Based on Thermodynamic Calculations

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Abstract

Thermodynamic calculations were performed to determine the optimal conditions for the growth of germanium epitaxial layers from a Ge-Sn solution (system) to a germanium substrate. The determination of the optimal conditions was based on the change in the Gibbs energy values of the system during the crystallization process and the size of the crystal-forming nanoclusters. Based on the results obtained, we determined the optimal conditions for obtaining low-dislocation, crystalline perfect germanium epitaxial layers from a liquid tin solution, and recommended starting the crystallization process at 923 K and finishing at 800 K. When the temperature drops below 800 K, the formation of $Ge_{1-x}Sn_x$ epitaxial layers from the Ge-Sn solution was observed.

Keywords: *Epitaxial layer; dislocation; nanoclusters; activity coefficients.*

1. Introduction

It is essential to obtain low-dislocation germanium crystals that can be used in detectors of special devices used in IR spectroscopy analysis and in other electronic devices. Numerous studies have been conducted to obtain low-dislocation germanium crystals.

In Germanium single-crystals grown by the Czochralski method, dislocations have been studied to appear continuously from the front during growth and to spread to the crystal mass in specific crystallographic directions [1].

The dislocation structure of single-crystalline germanium crystals grown in the (211) and (110) directions by the Czochralski method has been studied using white light X-ray topography [2].

Obtaining solid semiconductor solutions with micro and nanosized based on group IV periodic systems such as SiGe, SiC, SiSn, GeSn, and SiGeSn is an urgent task due to their specific electrophysical and photoelectric properties. Especially, optoelectronic devices operating in the infrared region of the spectrum are in demand, which is built on the basis of photo and heat-sensitive materials with a narrow band gap.

Semiconductor solid solution $Ge_{1-x}Sn_x$ is a narrow-gap material and has great potential for the development of infrared photodetectors. germanium and tin do not react under ambient conditions, i.e. are sustainable. And also, $Ge_{1-x}Sn_x$ is an attractive semiconductor material for Photonics, but the low solubility of tin in germanium limits its growth. To obtain a high Sn content in $Ge_{1-x}Sn_x$, it is usually grown at a low temperature, which would lead to inevitable dislocations. $Ge_{1-x}Sn_x$ was laterally grown by the fast melting method and the lattice parameter matched the size of the germanium lattice parameters [3].

The possibility of growing single-crystal $Ge_{1-x}Sn_x$ on a silicon substrate was shown in [4] using plasma chemical vapor deposition (PE-CVD). The density of dislocations in the substrate Si-$Ge_{1-x}Sn_x$ film heterointerface was~10^9 cm^{-2} due to the lattice mismatch between them.

A $Ge_{1-x}Sn_x$ alloy with a thickness of 250 nm was grown on a germanium (001) substrate by molecular beam epitaxy at low temperatures. The microstructures of $Ge_{1-x}Sn_x$ samples were studied by transmission and scanning electron microscopes. The results show that defects are mainly localized at the $Ge_{1-x}Sn_x$/Ge interface [5].

It was experimentally established in [6] that the temperature required for crystallization of $Ge_{1-x}Sn_x$ is reduced, and the crystallinity is improved compared to the case of pure germanium. In $Ge_{1-x}Sn_x$ film deposition, there is an optimal tin composition for the best crystalline after relaxation at temperatures t°<500°C, when seed growth prevails over nucleation. Thin films of $Ge_{1-x}Sn_x$ alloys containing up to 8.7 at. % tin grows at low crystallization temperatures of 370~470°C on silicon. The direct band gap is significantly red limit from 0.8 eV for pure germanium to ~0.5 eV for crystalline $Ge_{0.913}Sn_{0.087}$. The authors believe that the obtained highly crystalline $Ge_{0.913}Sn_{0.087}$ thin films on SiO_2 were obtained by the crystallization of a sample of 9.5 at. % tin is an important step towards growing a low defect density close to single-crystal $Ge_{1-x}Sn_x$ on amorphous materials [6].

To obtain plastically relaxed $Ge_{1-x}Sn_x$ layers using the technological method of molecular beam epitaxy to grow on silicon, without using an intermediate germanium buffer layer, a discrepancy was caused due to differences in the lattice parameters of the Si/$Ge_{1-x}Sn_x$ hetero compound materials [7].

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Given the narrow band gap of $Ge_{1-x}Sn_x$ can be adjusted by adding tin content, and $Ge_{1-x}Sn_x$ material can be applied to light-emitting devices, including laser and LED. The indirect band gap of $Ge_{1-x}Sn_x$ passes to the direct band gap due to an increase in the concentration of the substituting tin in the germanium lattices [8].

Using ion implantation and pulsed laser melting (PLM), $Ge_{1-x}Sn_x$ layers 0.2 μm thick with different atomic concentrations of 0.5 % to 3.0 % were obtained. The implanted germanium layer becomes amorphous due to bombardment with high kinetic energy tin ions. The re-growth of the $Ge_{1-x}Sn_x$ layer after PLM and the expansion of the lattice were confirmed by X-ray diffraction and micro-Raman spectroscopy. Studying morphology and chemical composition of $Ge_{1-x}Sn_x$, the authors confirmed the single-crystal structure of the alloys [9].

Paper [10] shows the production of $Ge_{1-x}Sn_x$ films by molecular beam epitaxy on germanium (001) substrates. The dependence of growth temperature and the effect of post-growth annealing were studied. We also carried out thermodynamic calculations, during film growth from a solution-melt, and in solid-liquid contact. The energy change of the liquid-solid interface during growth is shown. Dissolved germanium is recrystallization from the volume of the Ge-Sn melts solution by the method of liquid-phase epitaxy.

Increasing the Sn content in the $Ge_{1-x}Sn_x$ alloy improves charge carrier mobility and converts the band gap from indirect to direct. However, the production of $Ge_{1-x}Sn_x$ is limited due to the equilibrium solubility of tin in germanium (no more than 1 at. %). Therefore, the authors of [11] tried to obtain planar $Ge_{1-x}Sn_x$ nanowires catalyzed by tin nanoparticles to overcome this limitation, reaching a nonequilibrium tin concentration of 22 at. %.

In our previous work, we reported that on the basis of experiments we managed to obtain epitaxial layers $Ge_{1-x}Sn_x$ in the temperature range 740÷450ºC [12].

To grow crystalline perfect germanium epitaxial layers, we performed thermodynamic calculations of the Ge-Sn solution. We aimed to determine energy-efficient growth regimes using Gibbs energy calculations and size analysis of crystal-forming nanoclusters.

2. Theoretical Part

To determine the optimal conditions for the growth of $Ge_{1-x}Sn_x$ crystals, calculations were performed based on experimental results. The application of calculations to real processes is of great practical importance. To do this, it is necessary to express the concentrations of tin and germanium components in terms of activity. We relied on the Clausius-Clapeyron and Gibbs–Duhem equations to determine the activity of the tin and germanium components in the system [13, 14].

$$\ln\left(\frac{1}{\gamma_{Ge}X_{Ge}}\right)=\frac{\Delta H_f}{R}\left(\frac{1}{T_c}-\frac{1}{T_l}\right) \tag{1}$$

$$\ln\gamma_{Sn}=-\frac{X_{Ge}}{X_{Sn}}(\ln\gamma_{Ge}-1) \tag{2}$$

Where X- is the concentration (mole fraction) of the component in the system, γ- is the activity coefficient, T_c- crystal formation temperature (K), T_l- liquidus temperature (K), ΔH_f is the heat of fusion (J/mol), R-universal gas is constant.

Activity (a) values were determined based on the determined activity coefficients of the germanium and tin components in the system. Using the activity values, the Gibbs energies of the mixing of germanium and tin components in the system at different temperatures were calculated. This allows you to get closer to the real process situations in the system. The mixing of Gibbs energy was determined using Eq. (3).

$$\Delta G_{mix}=RT(X_{Ge}\ln a_{Ge}+X_{Sn}\ln a_{Sn}) \tag{3}$$

Germanium nanoclusters were thought to be involved in crystal growth in the system.

Germanium nanoclusters in the system are located on the growing surface and form a crystallization process. Therefore, the total Gibbs energy of the crystallization process on the growing surface can be expressed as follows.

$$\Delta G_{system}=\Delta G_{cr}+\Delta G_{mix.then}-\Delta G_{mix.first} \tag{4}$$

Depending on the Gibbs energy of crystallization, the size of the 2D bulges that cause dislocations in the growing layer on the base surface is determined. The following equation was used to determine the size of the bumps.

$$\Delta G_{cr}=\frac{4\sigma^2 bV_m}{\Delta G_v} \tag{5}$$

Here σ- nanoclusters are the surface tension at the liquid tin boundary, b- 2D is the size of the bulges, V_m- is the molar volume, ΔG_v- is the volumetric Gibbs energy of the crystal.

Eq. (6) can be used to determine the volumetric Gibbs energy.

$$\Delta G_v=\Delta H_f\,\frac{T_l-T_c}{T_l} \tag{6}$$

Using the above calculation formulas, we will be able to determine the optimal conditions for crystal growth.

3. Experience Part

3.1. Equipment and Materials

Chemically pure samples of tin and germanium (Taizhou ATS Optical Material Co., Ltd.) were used for the experiment. Germanium plate in the <111> direction was used as the substrate. The experiments were carried out in an EPOS-type device (Pd-15T purifier) and in a hydrogen atmosphere at a temperature of 823÷1200 K. 4-Channel Type-K thermometer was used to check the temperature. An AE ADAM NBL 214e (Germany) analytical balance was used to measure the weight of the substances. An SEM EVO MA 10 (Zeiss) device was used to analyze the crystal surface.

3.2. Obtaining Crystals of Germanium

Experiments were carried out in an EPOS-type device (Pd-15T purifier) and in a hydrogen atmosphere at temperatures of 823÷1200 K to determine the solubility of germanium in the tin and to obtain germanium crystals.

The resulting crystal sample was treated with a dilute solution of hydrochloric acid. The surface of the processed crystal sample was examined using a scanning electron microscope.

4. Results and Discussion

The concentrations and activities of the components for the saturated state of the Ge-Sn system at temperatures 823÷1173 K were determined.

Activity coefficients were determined based on Eq. (1) and Eq. (2) based on the concentrations of the components corresponding to different temperatures (Table 1-2).

Table 1. Activity coefficient and activity values of germanium component in Sn-Ge system.

T, K	X_{Ge}	γ_{Ge}	a_{Ge}
1173	0.960	0.924	0.887
1123	0.850	0.882	0.750
1073	0.613	1.016	0.623
1023	0.386	1.317	0.509
973	0.233	1.746	0.407
923	0.166	1.9085	0.318
873	0.116	2.070	0.2415
823	0.085	2.0854	0.1773

Table 2. Activity coefficient and activity values of tin component in Sn-Ge system.

T, K	X_{Sn}	γ_{Sn}	a_{Sn}
1173	0.040	2.4360	0.0974
1123	0.150	0.7500	0.1125
1073	0.387	0.35845	0.1386
1023	0.614	0.30926	0.1896
973	0.767	0.31048	0.2380
923	0.834	0.32326	0.26937
873	0.884	0.33417	0.2952
823	0.915	0.3436	0.31438

Based on the determined results, the Gibbs energy values of the mixing of the components were calculated using Eq. (3).

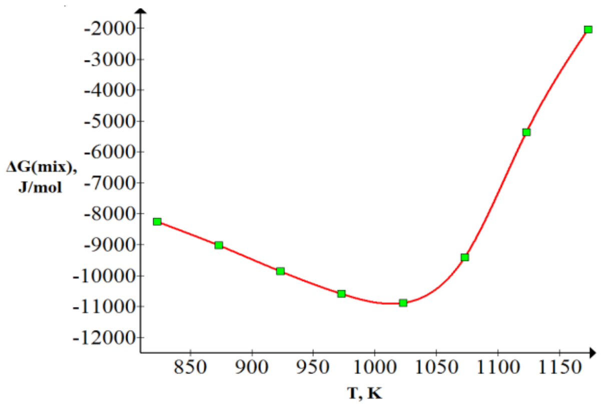


Figure 1. Temperature dependence of the Gibbs energy of mixing in the Ge-Sn system.

If we look at the graph in Figure 1, we can observe that the initial Gibbs energy values of the mixture are high when the temperature is high and decrease to a temperature of 1023 K. It is also observed that mixing the above components at temperatures below 1023 K increases the Gibbs energy values.

At the minimum Gibbs energy value of the mixture, the melting process of the components in the system is observed to be the highest. As a result, the increase in Gibbs energy values above the mixing temperature above 1023 K leads to the conclusion that the melting capacity of the components decreases. However, in the experiment, conversely, as the temperature increases, the solubility of germanium at tin increases. Using the results obtained, the following conclusion can be drawn. The germanium and tin components up to the minimum value of the Gibbs energy of the mixture conform to the basic law. Above 1023 K, a chemical change may be observed in the system.

It has been assumed that the main participants in the formation of germanium crystals from the Ge-Sn system are nano-sized particles. It is important to know the size of the nanoclusters that form germanium crystals. This is because the density of dislocations at the base-film boundary during the growth of $Ge_{1-x}Sn_x$ epitaxial layers on the substrate is directly related to the size of the crystal-forming nanoclusters.

When a large nanocluster is located on the crystal growing surface, it causes various defects to appear on the crystal surface. As a result, the density of dislocations on the surface increases. It is therefore advisable to grow crystals in the presence of small-sized nanoclusters.

Based on data from the literature [15], the sizes of crystal-forming nanoclusters were determined using the following Eq. (7).

$$r = \frac{2\sigma V_m}{\Delta G_V} \qquad (7)$$

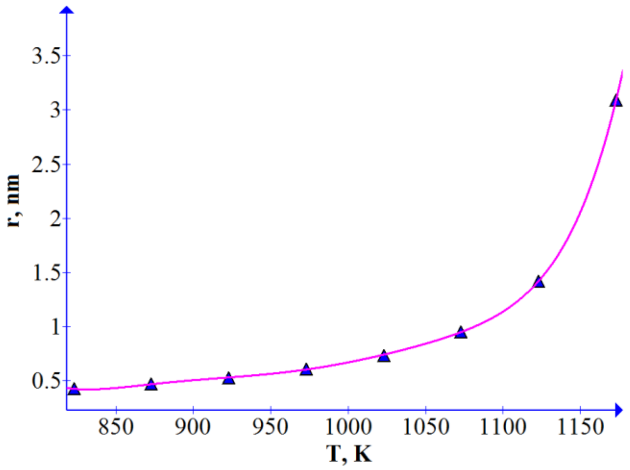


Figure 2. Temperature dependence of the size of germanium nanoclusters.

At low temperatures, the size of germanium nanoclusters involved in crystallization decreases.

The analysis of the results showed that the differences in the size (radius) of the germanium nanoclusters forming crystals below the temperature of 923 K were reduced (Figure 2). Small germanium nanoclusters form low-dislocation and crystalline perfect epitaxial layers.

The formation of germanium nanoclusters involved in the crystallization process is the basis for determining the optimal state of crystal formation in the system by determining the critical Gibbs energies. The critical Gibbs energies of crystal-forming nanoclusters were determined at different temperatures.

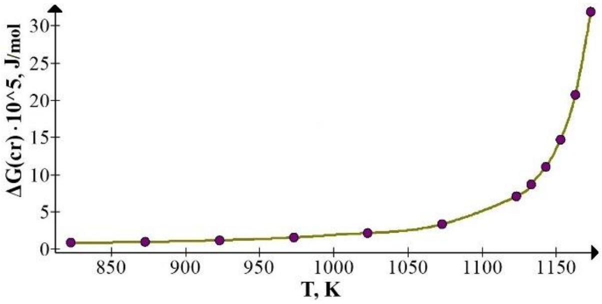


Figure 3. Critical Gibbs energies of germanium nanoclusters.

As can be seen from the graph, the differences between the critical Gibbs energy values of the crystal-forming germanium nanoclusters decrease sharply below a temperature of 923K (Figure 3). That is, the change of critical Gibbs energy values of nanoclusters is linear. It is significant that at temperatures below 923 K the values of the critical Gibbs energy are low and the differences between the values are small. A low value of Gibbs energy means that less work is done to form nanoclusters under the same conditions.

It is very important that the sizes of the nanoclusters involved in the crystal formation are close to each other in the temperature range of the critical Gibbs energy.

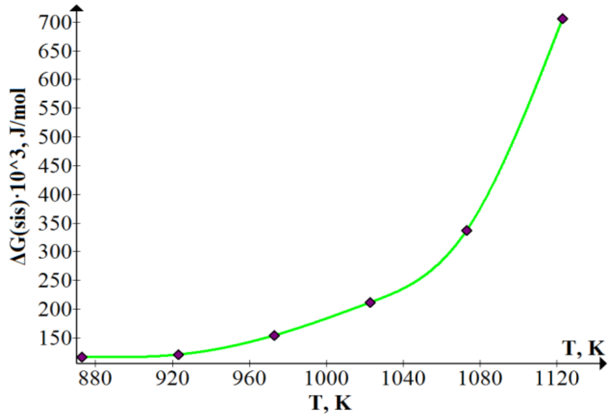


Figure 4. Temperature dependence of the Gibbs energy of a system during crystallization (With the participation of nanoclusters).

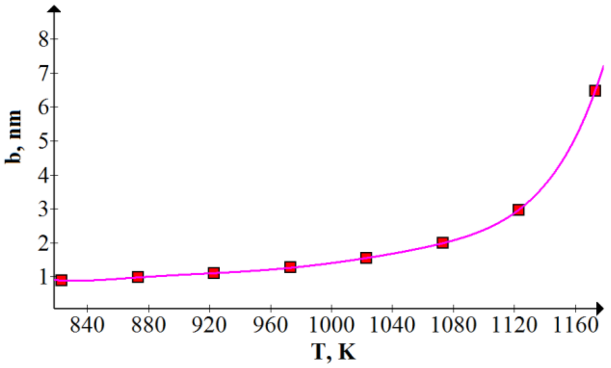


Figure 5. Temperature dependence of the size of the 2D bulges of the germanium crystal growing from the liquid tin solution to the germanium substrate.

As the initial crystallization temperature of the growing germanium crystal in the substrate decreases, the size of the 2D bumps on the growing surface decreases due to the small size of the germanium nanoclusters involved in crystallization. The dimensions of the 2D bumps were calculated using Eq. (5). In the high-temperature ranges of crystallization, the difference between the bulge sizes is large, and the difference between the values decreases with decreasing temperature. As the temperature began to decrease from 923 K, the differences between the values of the 2D bulge sizes decreased sharply (Figure 5). It is desirable that the initial growth temperature be less than 923 K to obtain perfectly crystalline, low-dislocation germanium crystals. If germanium crystals are grown from tin solution at temperatures below 800 K, a solid mixture with an epitaxial layer of $Ge_{1-x}Sn_x$ is formed [12]. The following are images of the $Ge_{1-x}Sn_x$ epitaxial layers formed under these conditions obtained using a scanning electron microscope (SEM) (Figure 6-7).

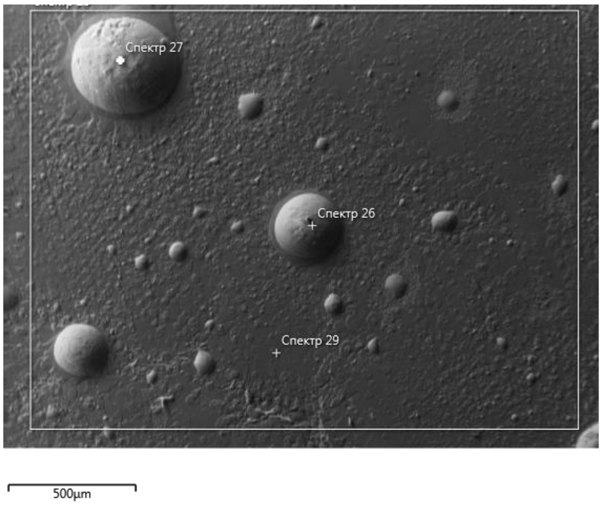
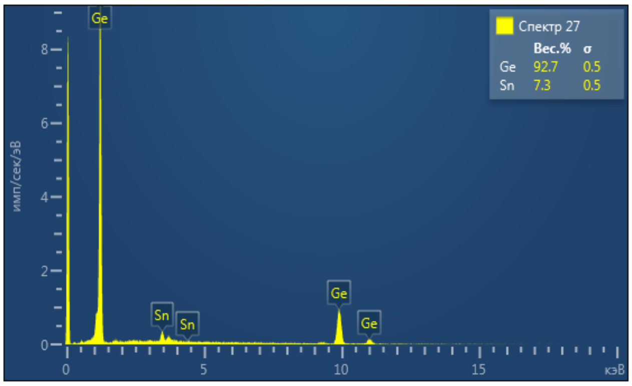


Figure 6. SEM image of the surface of epitaxial layers of $Ge_{1-x}Sn_x$ solid mixture.



Спектр 27	Вес.%	σ
Ge	92.7	0.5
Sn	7.3	0.5

Figure 7. Quantitative composition of elements in the epitaxial layers of $Ge_{1-x}Sn_x$ solid mixture.

The analysis process was performed at SEM EVO MA 10 (Zeiss). The sample obtained for analysis was treated using a hydrochloric acid solution. The purpose of processing is to remove tin particles that are mechanically located on the surface. If we look at the results of the analysis, we can see the data indicating the formation of epitaxial layers of $Ge_{1-x}Sn_x$ solid mixture on the growing surface below a temperature of 800 K. It was found to contain 92.75 % germanium and 7.25 % tin in terms of mass.

5. Conclusion

Based on the results obtained, the optimal conditions for obtaining low-dislocation, crystalline perfect germanium epitaxial layers from a liquid tin solution were determined. The determination of the optimal conditions was based on the change in the Gibbs energy values of the system during the crystallization process and the size of the crystal-forming nanoclusters.

We found that one of the reasons for the relatively high density of dislocations in crystals grown at high temperatures was related to the size of the nanoclusters.

We recommend starting the crystallization process from 923 K and ending at 800 K. At temperatures below 800 K, the formation of $Ge_{1-x}Sn_x$ epitaxial layers is observed.

Nomenclature

a	Activity
γ	Activity coefficient
ΔG_{mix}	The Gibbs energy of mixing, J/mol
ΔG_v	Volumetric Gibbs energy
ΔG_{cr}	Critical Gibbs energy, J/mol
R	Universal gas constant, 8.314 $J \cdot K^{-1} \cdot mol^{-1}$
T	Temperature, K
X	Mole fraction
σ	solid-liquid surface tension, J/m^2
V_m	Molar volume, m^3/mol
ΔH_f	Heat of fusion, J/mol
b	2D is the size of the bulges, m
r	nanocluster radius, m

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