

Thermodynamic determination of optimal conditions for growing Si_{1-x}Ge_x crystals from a tin solution on a silicon substrate

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1. Introduction

Abstract

Thermodynamic calculations have been carried out for growing crystalline Si_{1-x}Ge_x solid solution epitaxial films on Si<100> and Si<111> substrates from a tin solution-melt by liquid-phase epitaxy. Nanoclusters are thought to be involved in crystal growth. To determine the optimal conditions for obtaining a Si_{1-x}Ge_x crystal from a Si-Ge-Sn solution system, we focused on the change in Gibbs energy and the size of the nanoclusters involved in crystal formation. On this basis, a film with a thickness of 5 µm to 8 µm was experimentally obtained in the temperature range from T_{c.s}=1135 K (crystallization start temperature) to T_{c.t}=1023 K (crystallization termination temperature). It was also possible to reduce the dislocation density at the substrate-film boundary (up to 3×10^4 cm⁻²) and along the growth direction (film surfaces up to 8×10^3 cm⁻²). A method of thermodynamic prediction for obtaining semiconductor structures has been developed.

Semiconductors belonging to the class A^{IV}B^{IV}, A^{IIB}V^I, A^{III}B^V are widely used in semiconductor instrumentation, with their wellknown physical characteristics. Connections with the rapid development of modern micro and nanotechnology, the demand for semiconductor solid solutions and structures with specific electrophysical and photoelectric properties in a more expanded spectrum are relevant.

Therefore, to obtain such crystal-perfect (with the lowest dislocation densities) solid solutions and structures with unique properties, different technological methods and growth facilities are used.

Epitaxial Si_{1-x}Ge_x (0.02<x<0.05) layers were grown on a Si(001) substrate by liquid-phase epitaxy in the temperature range from 950°C to 750°C. The dislocation density was $N_d \approx 10^6$ cm⁻². But the grown film experiences tensile deformation after cooling to room temperature [1,2] in the literature, it is reported that an n-type Si_{1-x}Gex (0.7<x<1) monocrystalline film of the same composition was grown from a bismuth solution on a silicon substrate with an orientation of <111>. Due to the difference in the parameters of the silicon substrate and the growing Si_{0.3}Ge_{0.7} film crystal lattice (as_i=5.43Å; a_{Ge}=5.66Å), the dislocation density was determined to be N_d≈5 × 10⁷cm⁻².

The integration of germanium in silicon is relevant for the manufacture of high-performance, low-cost solar cells belonging to class III-V on silicon. In [3], epitaxial germanium was integrated on crystalline silicon (110) substrates by thermal annealing of amorphous germanium films as a monolithic one. This occurs through liquid-phase epitaxy when the germanium layer is heated in an inert atmosphere to a melting point of 937°C. Under slow forced cooling, Ge silicon (100)

was grown in the direction of the substrate and was found to form a 1 μm thick Ge epitaxial film with a dislocation density of $N_d \!\!\approx\!\! 10^9 cm^{-2}$ on Si.

Some authors have developed a thermodynamic model of the dependence of the density of threading dislocations (TDD) on the thickness of growing Ge, GaAs films with a mismatched lattice on Si(100) substrates. According to this model, the quasi-equilibrium TDD of a given strain-relieved film decreases in inverse proportion to the square of its thickness [4]. And also, comparative analyzes and simulations are given, the dependence of the dislocation density on the thickness of epitaxial layers during heteroepitaxial growth of films (at the substrate-film heterointerface $N_d \approx 10^{10}$ cm⁻² to 10^{12} cm⁻² and along the growth direction $N_d \approx 10^6$ cm⁻² to 10^7 cm⁻²) [5].

Epitaxial Si_{1-x}Ge_x layers with a gradient composition on Si at a temperature of 900°C were obtained both using molecular beam epitaxy and fast thermal chemical vapor deposition, with dislocation densities N_d= 3×10^6 to 5×10^4 [6].

 $Si_{0.973}Ge_{0.027}$ epitaxial layers were grown on a Si(001) substrate by lateral liquid phase epitaxy (LLPE) and this reduced the dislocation density to 10^3 cm⁻². But relatively small (x=0.027) Ge contents in the composition of $Si_{1-x}Ge_x$ have little effect on the electrophysical and photoelectric properties of the films; this will limit the great possibilities of their application in instrumentation [7].

The epitaxial layers of the Si_{1-x}Ge_x solid solution were grown by us from a limited volume of a tin and gallium solution-melt by the method of liquid epitaxy. Morphological and structural studies of the grown solid solutions showed that with increasing temperature, the onset of crystallization at the substrate-film boundary of the dislocation density (N_d) increases from 9.5×10^4 cm⁻² (at a temperature of 900°C) to 7.5×10^5 cm⁻² (at a temperature of 1050°C) [8].

However, those modes of technological growth, which are associated with the physical and chemical properties of the growing solution-melt and the thermodynamic equilibrium state of such a system, have not been studied enough so far. Based on theoretical thermodynamic calculations from the energy point of view of the solution-melt system, we managed to determine the optimal and lowcost mode of technological growth of epitaxial layers of Si_{1-x}Ge_x solid solutions from a limited tin solution-melt by liquid epitaxial.

This made it possible to experimentally obtain crystalline perfect epitaxial layers with the lowest densities of dislocations, defects, vacancies, and secondary phases on a Si substrate. The physicochemical nature of the optimal conditions for the growth regime is substantiated. Some thermodynamic parameters such as the activity coefficient of Si and Ge in a tin solution-melt are calculated based on previous experimental results. From the point of view of thermodynamic equilibrium conditions of a liquid system, a method has been developed for determining the optimal conditions for growing semiconductor solid solutions from a liquid phase.

2. Experimental

2.1 Materials and methods

Chemically pure samples of tin, germanium and silicon (Taizhou ATS Optical Material Co., Ltd.) were used for the experiment. Silicon plate in the <100> direction was used as the substrate.

The experiment was carried out in an EPOS-type device (Pd-15T purifier) and in a hydrogen atmosphere at a temperature of 1023 K to 1323 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. The composition of the components on the thickness of the crystal was determined using the device Jeol-JSM-LV1059 (Japan).

2.2 Theoretical calculations and predictions for obtaining crystalline perfect Si_{1-x}Ge_x films

The research was performed to determine the optimal conditions for the growth of $Si_{1-x}Ge_x$ epitaxial layers from a tin solution to a silicon substrate at the same cooling rate.

The thermodynamic parameters of the solution in terms of energy were analyzed based on experimental results in order to grow Si1-xGex epitaxial layers with crystal structural integrity and low dislocation density from a liquid phase tin solution to a relatively inexpensive silicon substrate and to achieve an optimal technological growth regime. To do this, the solubility values of the soluble components (Si, Ge) in the solvent (Sn) at the same temperatures were first determined. The compositional proportions of the Si and Ge components in terms of the thickness of the epitaxial layers of Si_{1-x}Ge_x grown during the crystallization process were determined using the Jeol-JSM-LV1059 (Japan) device (Figure 1). The composition of the solution at each temperature was determined by subtracting the amount of Si and Ge from the initial solution, which passed into the epitaxial layer during the crystallization process. From these results the saturated composition of the solution for each temperature becomes known (Table 1).

It is necessary to use the activity (a) values of the components to achieve more accurate results. For this purpose, the equations for determining the activity coefficients (γ) for the solution system Si, Ge and Sn were used [9].

$$RT \ln \gamma_{Sn} = \alpha_{Si-Sn} X_{Si}^2 + \alpha_{Ge-Sn} X_{Ge}^2 + (\alpha_{Si-Sn} + \alpha_{Ge-Sn} - \alpha_{Si-Ge}) X_{Si} X_{Ge}$$
(1)

$$RT \ln \gamma_{Si} = \alpha_{Si-Sn} X_{Sn}^2 + \alpha_{Si-Ge} X_{Ge}^2 + (\alpha_{Si-Sn} + \alpha_{Si-Ge} - \alpha_{Ge-Sn}) X_{Ge} X_{Sn}$$
(2)

$$RT \ln \gamma_{Ge} = \alpha_{Ge-Sn} X_{Sn}^2 + \alpha_{Si-Sn} X_{Si}^2 + (\alpha_{Ge-Sn} + \alpha_{Si-Ge} - \alpha_{Si-Sn}) X_{Si} X_{Sn}$$
(3)

Where X is the mole fraction, R is the universal gas constant, $\alpha_{Si-Sn}=6410$, $\alpha_{Si-Ge}=1615$, $\alpha_{Sn-Ge}=735$, T temperature (K).



Figure 1. Distribution of components over the thickness of the graded-gap $Si_{1-x}Ge_x$ epitaxial layer.

Table 1. The composition of the selected Si-Ge-Sn solution at a temperature of 1323 K and the composition of the solution at temperatures suitable for the formation of $Si_{1-x}Ge_x$ epitaxial layers.

T, K	n(Si) (mol)	n(Ge) (mol)	n(Sn) (mol)
1323	3.900%	21.00%	75.10%
1273	3.480%	21.09%	75.43%
1223	3.0587%	21.1813%	75.76%
1173	2.641%	21.265%	76.094%
1123	2.243%	21.328%	76.4297%
1073	1.88%	21.355%	76.7643%
1023	1.55874%	21.34126%	77.100%

Т, К	γsn	<i>a</i> _{Sn}	γsi	a _{Si}	γGe	<i>a</i> _{Ge}	
1323	1.00798	0.757000	1.5522	0.0605358	1.028152	0.21591	
1273	1.007688	0.76008596	1.58557	0.05519052	1.030633	0.217365	
1223	1.007383	0.76319325	1.62255	0.04962867	1.0333706	0.218881	
1173	1.007076	0.76632226	1.66367	0.04393697	1.0363775	0.220388	
1123	1.006782	0.76947335	1.70946	0.03834318	1.0396411	0.2217347	
1073	1.00652	0.77264826	1.76056	0.03310274	1.0431415	0.2227674	
1023	1.00630	0.77585140	1.81789	0.02833609	1.0468816	0.2234239	

Table 2. Temperature appropriate values of activity coefficients of tin, silicon and germanium components.

To find the optimal conditions for the crystallization process, it is necessary to determine the change in the Gibbs energy of the system. We focused on the change in Gibbs energy (ΔG_{cr}) in the formation of a critical-sized nanocluster that initiates the crystallization process. We determine the change in Gibbs energy of a system during crystallization from the following Equation (4) [10,11]:

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

Here ΔG_{cr} -crystal formation is a change in Gibbs energy, $\Delta G_{mix,first}$ mixing of components in a first-order solution is a change in Gibbs energy, $\Delta G_{mix,fhen}$ - mixing of components in a solution is a change in Gibbs energy.

We found the change in the Gibbs energy of the crystal-forming nanoclusters from Equation (5). Using this equation, we determine the Gibbs energy required to overcome the energy that hinders the crystallization process [12,13]:

$$\Delta G_{\rm cr} = \frac{16\pi\sigma^3 V_{\rm m}^2}{3(\Delta G_{\rm v})^2} \tag{5}$$

We determined the Gibbs energies for mixing the Si, Ge, and Sn components in a solution system according to their composition at defined temperatures from Equation (6) [10,14]. To make the results specific to real solutions, the activity values of the components were used, rather than the concentration values (Table 3).

$$\Delta G_{\text{mix}} = \text{RT}(X_{\text{Si}} \ln a_{\text{Si}} + X_{\text{Ge}} \ln a_{\text{Ge}} + X_{\text{Sn}} \ln a_{\text{Sn}})$$
(6)

From the results obtained, it can be seen that as the temperature decreases (initially, from the crystallization temperature), the mixing Gibbs energy increases linearly (ΔG =(-0.0073·T+2.679) × 10³ J·mol⁻¹). This change indicates a decrease in the solubility of the components in the solution system (Figure 2).

Using the detected data, the change in the Gibbs energy of the system during crystallization was found based on the formula (4) (Figure 3).

It is clear from the graph that during the crystallization process, the specific Gibbs energy change of the system was observed to correspond to 1173 K to 1183 K. We assumed that this temperature range was the optimal condition for the growth of the $Si_{1-x}Ge_x$ film, and this in temperature, we grew the $Si_{1-x}Ge_x$ epitaxial layers from the tin solution to the Si<100> and Si<111> substrates (Figure 4). The results obtained in the experiment confirmed the above conclusions. Under these conditions, the epitaxial layers of the $Si_{1-x}Ge_x$ solid mixture formed a crystal with low dislocation (3×10^4 cm⁻² at the substrate-based boundary and 8×10^3 cm⁻² at the film surface).

Table 3. Temperature-appropriate values of Gibbs energy of mixing of tin, silicon and germanium components.

Т, К	$\Delta G_{mix} (J \cdot mol^{-1})$		
1323	$-7.04360574 \times 10^{3}$		
1273	$-6.663872948 \times 10^{3}$		
1223	$-6.2877651669 \times 10^{3}$		
1173	-5.9163794×10^{3}		
1123	$-5.55237462 \times 10^{3}$		
1073	$-5.175082476 \times 10^{3}$		
1023	$-4.857060674 imes 10^3$		



Figure 2. Temperature dependence of Gibbs energy of mixing of components in Si-Ge-Sn solution system.



Figure 3. The change in the Gibbs energy of a system during the crystallization of $Si_{1-x}Ge_x$.



Figure 4. Dislocations on the surface of the $Si_{1-x}Ge_x$ epitaxial layers grown on the Si <111> substrate.



Figure 5. Temperature dependence of the change of Gibbs energies in the crystallization process of silicon and germaniums.



Figure 6. Temperature dependence of the size of silicon and germanium nanoclusters involved in crystal formation.

However, the change in the Gibbs energy of the system during the crystallization of Si and Ge in solution is as follows. It was assumed that Si and Ge do not interact with each other in terms of energy.

By analyzing the obtained graphic results, we found that the change in the Gibbs energy of the system during the crystallization of Si and Ge at a temperature of 1183 K is the same (Figure 5). At this temperature, we assume that the potential for Si and Ge to grow from the solution at the Si base is close.

In addition to knowing the optimal value of the change in Gibbs energy for the crystallization process, it is necessary to take into account the particle size formed in the system. This is because the formation of defects and dislocations in the crystallization of Si and Ge from a solution of Sn depends on the size of the crystalline particles. Therefore, we determined the crystal-forming particle sizes at temperatures at which Si_{1-x}Ge_x solid mixture epitaxial layers can be grown [15-17]. From the graph, the change in the radius size of silicon and germanium nanoclusters at different temperatures is shown as $r=4\cdot10^{-8}\cdot T^{4}$ - $0.0002\cdot T^{3}+0.2652\cdot T^{2}-192.62\cdot T+52436$ (R²=0.999) and $r=5\cdot10^{-6}\cdot T^{2}$ - $0.009\cdot T+5.4842$ (R²=0.999) (Figure 6).



Figure 7. Computational results of Si from X-ray diffractogram of epitaxial layers of $Si_{1-x}Ge_x$ solid mixture grown on Si substrate.



Figure 8. Computational results of Ge from X-ray diffractogram of epitaxial layers of $Si_{1-x}Ge_x$ solid mixture grown on Si substrate.

At 1133–1135 K, the radii of the Si and Ge particles involved in crystallization have almost the same values. It was concluded that $Si_{1-x}Ge_x$ single crystals with relatively low defects and dislocations could be grown at these temperatures. This is because the probability of dislocations is sharply reduced when particles of the same size settle on the substrate surface.

Based on the above results, at a temperature of 1135 K (initial crystallization temperature) to 1023 K (final crystallization temperature), epitaxial layers of a solid mixture of $Si_{1-x}Ge_x$ from a tin solution were grown on a Si<100> and Si<111> substrates. When studying the morphology of the obtained crystal samples, a sharp decrease in the density of dislocations was observed both in the direction of growth of the epitaxial layers at the base-film boundary. However, due to the small temperature range, a thin crystalline layer (5 µm to 8 µm) is formed.

In the experiment, X-ray phase analysis was performed to determine the structure of the epitaxial layers of the grown Si_{1-x}Ge_x solid mixture.

X-ray phase analysis was performed on XRD-6100 Shimadzu X-ray diffractometer (λ =1,540598Å, Cu-Ka1). The obtained diffractograms were analyzed in Match!3. Analysis of the data showed that the size of the base and the unit crystal lattice of the first Si grown on it was a=5.43 Å (α =90°, β =90°, γ =90°), and the shape of the crystal lattice was found to be cubic (Fd-3m) (Figure 7). During the crystal growth process, it was found that silicon was initially formed in the intermediate layers with a variable content of Si_{1-x}Ge_x and the surface layer with Ge. The crystal lattice size of Ge in the surface layer was a=5.66 Å (α =90°, β =90°, γ =90°), and the crystal lattice shape was found to be cubic (Fd-3m) (Figure 8). The crystal lattice sizes of the Si_{1-x}Ge_x epitaxial layers in the intermediate layer averaged a=5,537 Å.

4. Conclusions

The energetically optimal conditions for the growth of lowdislocation $Si_{1-x}Ge_x$ epitaxial layers from the Si-Ge-Sn solution system to the silicon substrate were determined using experimental results and theoretical calculations. Under defined optimal conditions, $Si_{1-x}Ge_x$ epitaxial layers were grown in a low dislocation state. We recommend 2 different optimum temperatures for crystal growth. It is necessary to start the process of growing from a temperature of 1183 K to obtain thicker (10 µm to 50 µm) epitaxial layers, and from 1135 K to obtain thinner (5 µm to 8 µm) epitaxial layers.

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