

## FEATURES OF GROWING Si- AND Si<sub>1-x</sub>Ge<sub>x</sub>-SINGLE-CRYSTAL FILMS FROM SOLUTION-MELT BASED ON TIN

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The features of variband single-crystal structures based on Si<sub>1-x</sub>Ge<sub>x</sub> ( $0 < x < 1$ ), which have been grown on Si(111) substrates from a tin solution-melt by liquid-phase epitaxy have been experimentally investigated and analyzed. A mechanism for the growth of such structures is proposed, and the reason for the greater thickness of the deposited films on the upper substrates for liquid-phase epitaxy is explained based on the Rayleigh–Taylor instability phenomenon. Optimal technological regimes for obtaining epitaxial layers and structures are predicted.

**Key words:** epitaxy, solution-melt, substrate, Rayleigh–Taylor instability, Brownian motion, diffusion.

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### I. INTRODUCTION

Obtaining high quality thin films of semiconductor materials with desired electro physical and photoelectric properties is a very important modern task [1–4]. One of the methods for obtaining such films is the method of liquid-phase epitaxy, where the features of film deposition processes have not yet been studied enough.

At present, heterostructures based on silicon, germanium, and  $A^{\text{IV}}B^{\text{IV}}$  type solid solutions are used to create semiconductor devices. Such heterostructures have a significant drawback, which consists in a mismatch between the lattice parameter  $a$  and the thermal expansion coefficients  $\alpha$  (TEC) of the substrate and crystallized layer ( $a_{\text{Si}} = 0.5431$  nm,  $a_{\text{Ge}} = 0.5658$  nm,  $\alpha_{\text{Si}} = 5.1 \cdot 10^{-6} \text{K}^{-1}$ ,  $\alpha_{\text{Ge}} = 6.1 \cdot 10^{-6} \text{K}^{-1}$ ). As a result, many defects can form in the film [5–8].

By smoothly changing the composition of Si<sub>1-x</sub>Ge<sub>x</sub> solid solution, it is possible to control some parameters, such as the band gap and spectral photosensitivity region. The synthesis of a silicon-germanium solid solution combines the regions of spectral photosensitivity of both silicon and germanium. Therefore, variband (Si<sub>1-x</sub>Ge<sub>x</sub>)-solid solution should have a wider region of spectral photosensitivity, which is important for the manufacture of photoelectric devices. In addition, the above solid solution can serve as a buffer layer in the production of films which grown in the sequence Si → Si<sub>1-x</sub>Ge<sub>x</sub> → GaAs, Si → Si<sub>1-x</sub>Ge<sub>x</sub> → (Si<sub>2</sub>)<sub>1-x-y</sub>(Ge<sub>2</sub>)<sub>x</sub>(GaAs)<sub>y</sub>, Si → Si<sub>1-x</sub>Ge<sub>x</sub> → (Ge<sub>2</sub>)<sub>1-x</sub>(InP)<sub>x</sub>. Such films have a lower defects density in the crystal structure than films grown using various methods without using a buffer layer [9, 10].

In the process of growing Si<sub>1-x</sub>Ge<sub>x</sub> epitaxial layers from the liquid phase, silicon substrates are traditionally used. This is due to the fact that both the

lattice parameter and TEC in a silicon substrate and the obtained epitaxial layers are close. It should be noted that the technological parameters of growing films from a solution-melt in such systems have not been sufficiently studied so far. The reason for this is that these parameters are determined both by the physicochemical properties of the solution-melt itself and by the technological features of the installations used. Therefore, the aim of this study is to analyze the mechanisms of the deposition and growth processes in order to explain the structural features of the grown epitaxial layers.

### II. MATERIALS AND METHODS

A variband solid solution ( $0 < x < 1$ ) was grown in a vertical-type quartz reactor with horizontally arranged substrates on an EPOS-type setup according to the procedure described in [11]. The study of the chemical composition of the cross section of the grown Si<sub>1-x</sub>Ge<sub>x</sub> epitaxial layers was carried out using a Jeol JSMLV-1059-Japan X-ray microanalyzer. XRD studies were carried out using a modernized D2 PHASER diffractometer (filtered CuK<sub>α</sub> radiation).

### III. DISCUSSION

In this work, variband solid solution films were obtained at different gap sizes between the upper and lower substrates. The variband properties of the solid solution was previously confirmed using SEM and XRD studies [9, 11]. It was found that the amount of silicon decreased monotonically with an increase in the distance from the substrate, while the amount of germanium increased



monotonically. The lattice parameter of the solid solution also changed monotonically, increasing from  $a_{\text{Si}} = 0.5431$  nm to  $a_{\text{Ge}} = 0.5658$  nm.

All films obtained with changing the gap  $d$  (changing the volume of the solution-melt between the substrates) had a typical feature. Under the same growth conditions (in particular, at the same temperature of the onset of crystallization  $T_{\text{sc}}$ ), the thicknesses of the films on the upper and lower silicon substrates changed quite significantly (Fig. 2). However, with a gap not exceeding 1.2–1.5 mm ( $d < 1.5$  mm), the layers grown on both substrates practically did not differ either in thickness or in the degree of the crystalline perfection. With an increase in the gap ( $d > 1.5$  mm), thicker and lower quality layers were formed on the upper substrates compared to lower ones. According to the authors of [12], this is due to diffusion and convection flows of components in a limited volume of the solution, provided that the density of the dissolved components is lower than the density of the solvent. This interpretation is not entirely clear.

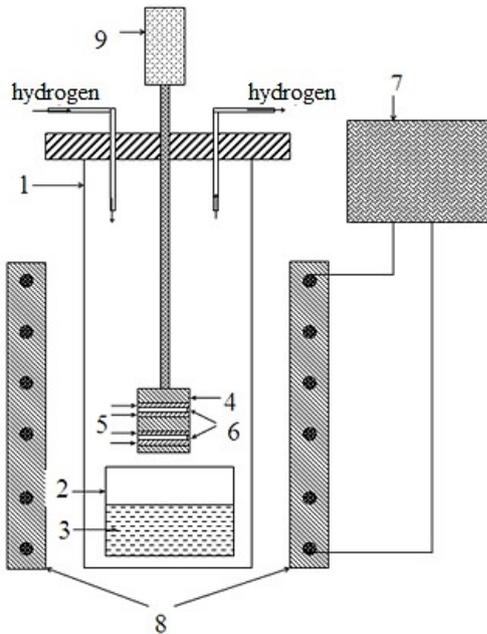


Fig. 1. Schematic diagram of the setup for liquid-phase epitaxy. 1 – quartz reactor, 2 – quartz crucible, 3 – solution-melt, 4 – graphite cassette, 5 – silicon substrates, 6 – graphite props, 7 – control unit, 8 – thermal unit and 9 – electric motor [11]

Similar regularities in the thickness and quality changes of the films as a function of the gap width were also observed at other values of  $T_{\text{sc}}$ . It should be noted that in order to select a certain value of the film crystallization onset temperature, it is necessary to correct the chemical composition of the solution-melt. In the case of an increase in  $T_{\text{sc}}$ , the amount of silicon and germanium in the melt should be increased according to the phase diagrams of Si–Sn and Ge–Sn [13, 14].

Analyzing these diagrams, it is easy to see that the liquidus temperatures decrease monotonically with an increase in the tin content in the melt. Moreover, when the content of tin is more than 80 at.%, the rate of

decrease in the liquidus temperature rapidly increases.

Consider the binary Si–Sn diagram as more visual. To explain the experimentally observed difference in the thicknesses of the layers deposited on the upper and lower substrates, a model experiment was carried out to grow pure silicon on silicon substrates (Fig. 2).

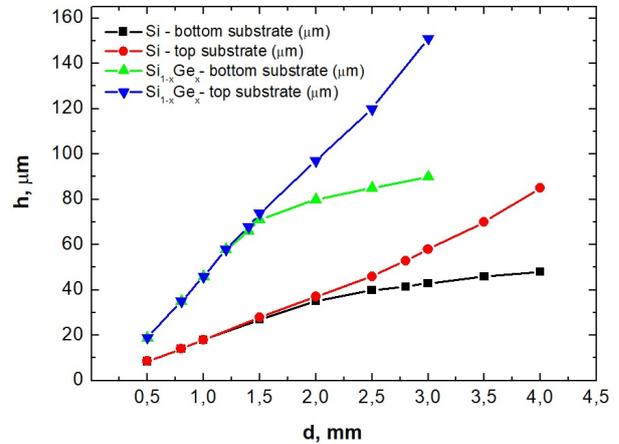


Fig. 2. Dependence of the thickness  $h$  of the epitaxial layers on the value  $d$  of the gap between the substrates obtained from the tin solution-melt ( $T_{\text{sc}} = 1323$  K for both melt solutions,  $T_{\text{fc}} = 873$  K and  $T_{\text{fc}} = 1053$  K for silicon and silicon-germanium melt solutions, respectively)

Let us analyze the dependence of the thickness of the layers deposited on the upper and lower substrates on the distance between the substrates. It is easy to see that the curves on both graphs have a similar form. Depending on the chemical composition of the melt (and hence on the temperature of the onset of crystallization) at a certain (“critical”) distance between the substrates, the thickness of the layers deposited on both substrates will be approximately the same. An increase in the distance between the plates above the critical one leads to the fact that the thickness of the layer deposited on the upper plate becomes larger.

It can be seen from the Si–Sn phase diagram that at high temperatures, which corresponds to the onset of the deposition process ( $T_{\text{sc}}$ ), the values of the temperature coefficient of silicon solubility in tin will be much higher than at the final temperatures of the process ( $T_{\text{fc}}$ ). Hence it follows that the maximum supersaturation of the melt with silicon and the possible formation of silicon clusters will occur at the initial stages of deposition.

Purely diffusion processes cannot ensure the formation of layers of different thicknesses on the upper and lower substrates. Therefore, let us try to explain the observed effect in terms of the cluster structure of the solution-melt.

Let us assume that at low cooling rates of the solution-melt used in the experiment ( $\approx 1$  K/min), a certain constant undercooling  $\Delta T$  is achieved, which acts as a thermodynamic stimulus for the formation of stable Si clusters. In our opinion, during the process of cooling the solution-melt (several hours at a cooling rate of 1 K/min), all silicon clusters contained in the volume between the plates, the distance between which is smaller

than the critical one, have time to reach the silicon substrates and settle on them (crystallize). Using the well-known equations for the diffusion of Brownian particles  $\langle x^2 \rangle = 2D\tau$  and the Stokes–Einstein equation  $D = kT/6\pi\eta R_c$ , as well as setting  $\langle x^2 \rangle = d^2$ , we can obtain an equation for estimating the radius of the clusters that can be deposited on the substrates during the cooling time  $\tau$ :

$$R_c = \frac{kT\tau}{3\pi\eta d^2},$$

where  $\langle x^2 \rangle$  is the average square of the displacement of a Brownian particle;  $D$  is the diffusion coefficient of a Brownian particle;  $\eta$  is the dynamic viscosity of the melt, whose value of which was calculated for each temperature from [15,16];  $R_c$  is the particle radius,

Estimations show that at the distance between the plates equal to 1.5 mm, as a result of random thermal motion all clusters with sizes  $\leq 15$  nm should have time to reach the upper or lower substrates with equal probability. The experimental fact that at a distance between the substrates smaller than the critical one, the thicknesses of the deposited layers on both substrates are the same indicates that the radii of the silicon nanoclusters existing in the melt solution under these conditions should not exceed 15 nm.

To specify the cluster size at a certain temperature, the structure of Sn<sub>86.5</sub>Ge<sub>12</sub>Si<sub>1.5</sub> melt was studied using the XRD method using a high-temperature diffractometer at temperatures of 900°C and 1050°C. As a result of the research, structure factors were obtained, by analyzing the first maximum of which it is possible to determine the size of clusters within the framework of the microheterogeneous structure of melts (Fig. 3).

The asymmetry of the first maximum of the structure factors indicates that two types of short-range order existed in the solution-melt (two types of clusters with different types of atomic ordering). Therefore, the first maxima were mathematically divided into two symmetrical peaks, whose profile was determined by the size of the clusters with different types of atomic ordering.

In our case, the first peak corresponds to the scattering of X-rays by tin-based microregions, and the second one, to those based on germanium and silicon.

Using the equation [17], we can determine the radius of the clusters

$$R_c = \frac{2\pi^3 n^2}{2.5^2 \Delta s},$$

where  $n$  is the number of the structure factor maximum,  $\Delta s$  is the width at half the height of the maximum.

According to the research results, it was found that at a temperature of 900°C, the size of tin clusters is about 1.28 nm, and the size of germanium or silicon clusters is about 0.630 nm. At a temperature of 1050°C, these parameters will be 1.23 nm and 0.821 nm, respectively.

Thus, the size of clusters in the solution-melt determined using the XRD method does not exceed the value of 15 nm obtained above. This can serve as confirmation that under the given conditions of deposition with a

distance between the plates  $\leq 1.5$  mm, all clusters, as a result of random thermal motion, should have time to reach the upper or lower substrates with equal probability.

It is known that in dispersed systems similar to the one under consideration, negative sedimentation processes can occur. A question arises: can the different thicknesses of the deposited layers on the upper and lower substrates be explained by this process?

According to [18], the path  $s$  traveled by dispersed particles can be calculated using the formula:

$$s = \frac{2(\rho_{Sn} - \rho_{Si})ga^2\tau}{9\eta},$$

where  $\rho_{Sn}$  is the density of the tin melt,  $\rho_{Si}$  is the density of silicon,  $g$  is the gravitational acceleration, and  $\tau$  is the time of the deposition process.

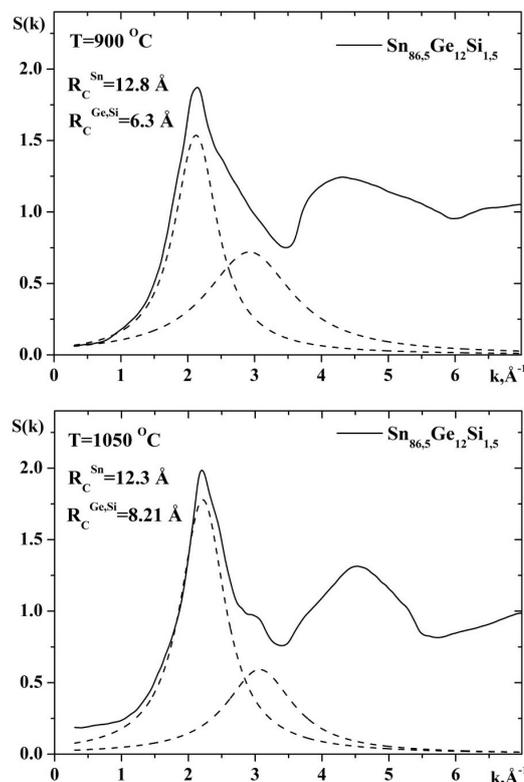


Fig. 3. Structure factors of the solution-melt Sn<sub>86.5</sub>Ge<sub>12</sub>Si<sub>1.5</sub>

The path calculated in this way for particles with a radius  $\leq 15$  nm does not exceed 0.5  $\mu\text{m}$ , which is much smaller than both the distance between the substrates and the difference between the thicknesses of the deposited layers. This suggests that the experimentally observed difference in the deposited layers at distances between the plates exceeding the critical value cannot be explained by the processes of negative sedimentation of clusters, since the role of these processes in the case under consideration will be negligibly small.

Thus, neither the diffusion processes of individual silicon atoms, nor the Brownian motion of clusters, nor

negative sedimentation processes can explain difference between the thicknesses of the deposited layers on the upper and lower substrates at distances between them exceeding the critical value. This difference in thickness can be explained on the basis of the following considerations. It is known [19] that the so-called transitional region is formed in the areas of the melt adjacent to the crystallization front. A typical feature of these areas is that they are supersaturated with silicon compared to the equilibrium composition of the solution-melt at a given temperature. However, this supersaturation will be smaller than in the regions of the melt that are far from the crystallization front. For the case of the Sn–Si melt, it is obvious that the density of the transition region due to the lower silicon content will be higher than the density of the main volume of the melt. It should be noted that a higher density of the melt near the upper substrate (compared to the density of the main volume) leads to the occurrence of processes typical of the Rayleigh–Taylor instability [20]: vertical

“flows” of liquids with different densities appear. Then the “flows” of the melt, enriched in silicon, rise up and provide accelerated growth of the deposited layer in certain places of the upper substrate. This can lead to the appearance of macroroughness on the surface of the deposited layer and ultimately cause a violation of the single crystallinity of the deposited layers. Silicon-depleted “flows” moving downwards will increase the thickness of the transition region near the lower substrate, thereby slowing down the deposition processes on it.

The studies of the morphology of the upper substrate at a distance between the plates slightly larger than the critical one (1.5 mm) showed the presence of “growths” in the form of blunt cones on the surface (Fig. 4,a). These formations may indicate the deposition of silicon at the points of collision between individual flows rising upward and the substrate. In this case, such a movement of individual thin flows can occur at insignificant thicknesses of the layer most oversaturated with silicon located in the middle areas between the substrates.

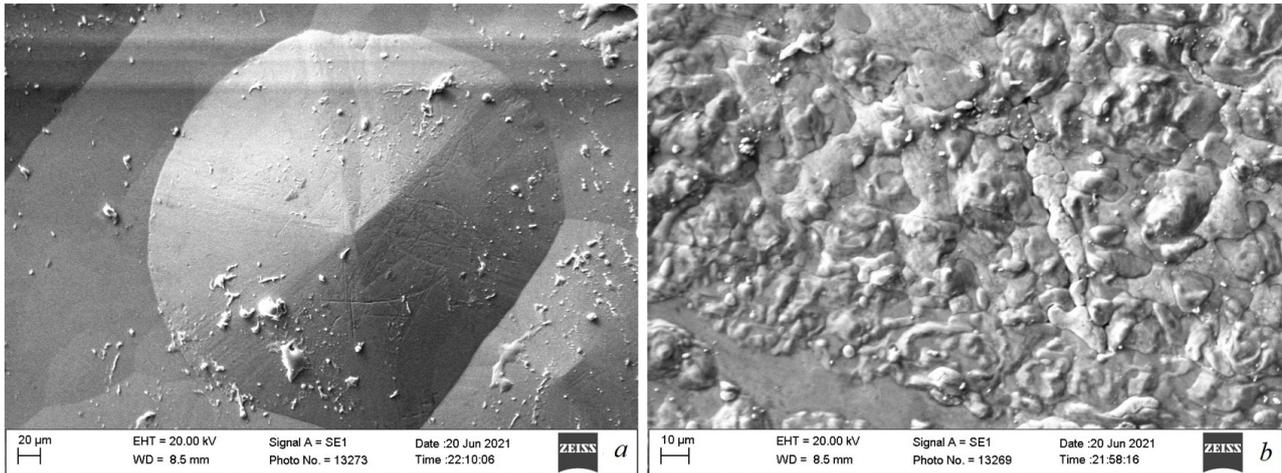


Fig. 4. Morphological features of the surfaces of the upper substrates at a distance between the plates of 1.6 mm (*a*) and 2.5 mm (*b*)

An increase in the distance between the substrates leads to an increase in the randomness of the flows. This results in the disappearance of individual thin flows. Eventually, there is a further decrease in the quality of the surface, leading to the disappearance of its single crystallinity (Fig. 4,b).

The fact that at distances between the substrates smaller than the critical one, the Rayleigh–Taylor effect does not appear can be explained as follows. At small distances between the substrates, the above-mentioned transition regions simply overlap, thereby excluding a significant density difference across the entire volume of the melt between the plates.

Thus, the greater thickness of the deposition layer on the upper substrate compared to the lower one, at distances between the plates exceeding the critical value, can be explained by the Rayleigh–Taylor instability. With a decrease in the temperature  $T_{sc}$  and the gap

size, the difference between the thicknesses of the layers deposited on both plates will decrease, and when the critical distance is reached, it disappears altogether due to the overlap of the transition regions. In this case, regions with noticeably different concentrations of components, which are a necessary condition for the Rayleigh–Taylor instability, disappear in the solution-melt.

#### IV. CONCLUSIONS

1. The experimental and theoretical evaluation of the cluster sizes in the solution-melt of the Si–Sn and Si–Ge–Sn systems at different temperatures showed that it is impossible to explain the difference in the thicknesses of the deposited silicon and germanium layers on the substrates in terms of sedimentation processes. The difference

between the thicknesses of the deposited layers on the upper and lower substrates in the process of growing coatings from a solution-melt at distances between the substrates exceeding the critical one is explained by the Rayleigh–Taylor effect.

2. To obtain high-quality deposited layers, it is necessary either to decrease the distances between

the plates below the critical ones, or to lower the cooling rate of the solution-melt.

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#### МОНОКРИСТАЛІЧНІ ПЛІВКИ З РОЗЧИНУ-РОЗПЛАВУ НА ОСНОВІ ОЛОВА

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Експериментально досліджено та проаналізовано особливості варізонних монокристалічних структур на основі твердого розчину Si<sub>1-x</sub>Ge<sub>x</sub> (0 < x < 1), вирощених на підкладках Si(111) з олов'яного розчину-розплаву методом рідкофазної епітаксії. Отримано плівки за різної величини зазору між верхньою та нижньою підкладками. Установлено, що з віддаленням від підкладки кількість кремнію монотонно зменшувалася, кількість же германію водночас монотонно зростала. Показано, що до деякої критичної величини проміжку між пластинами товщини плівок на обох підкладках практично не відрізнялися. Збільшення відстані вище від критичної приводило (за однакових умов зростання) до того що, на верхніх підкладках формувалися більш товсті й низькоякісні шари, ніж на нижніх. Показано, що пояснити цей експериментальний факт з погляду седиментаційних процесів неможливо. Різниця між товщинами вирощених шарів на верхній та нижній підкладках у процесі вирощування покриттів із розчину-розплаву за відстаней між підкладками, що перевищують критичну, пояснюється ефектом нестійкості Релея–Тейлора. Установлено, що для отримання якісних вирощених шарів потрібно розташовувати пластини на відстанях, що не перевищують критичні, або зменшувати швидкість охолодження розчину-розплаву.

**Ключові слова:** епітаксія, кристалізація, розчин-розплав, твердий розчин, підкладка, нанокластер, структура, нестійкість Релея–Тейлора, броунівський рух, дифузія.