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Studying the Growth Mechanisms of Si Epitaxial Layers from a Limited Volume of Si-Sn Solution Using Theoretical Calculations and the Sedimentation Method

Abstract. Differences in the thicknesses of the layers formed during the growth of solid solution epitaxial layers such as $Si_{1-x}Ge_x$, $(Si_2)_{1-x}(GaP)_x$, $(Ge_2)_{1-x}(GaAs)_x$ and $(Ge_2)_{1-x}(ZnSe)_x$ on horizontally placed top and bottom substrates from a confined volume of liquid solution based on programming cooling were determined. To study the cause of this situation, silicon crystal layers were grown from a limited amount of solution (Si-Sn) on horizontally placed Si substrates in the temperature range of 973-1323 K. In this process, a thicker crystal layer grew on the top substrate. The quality of the crystal layer grown on the top substrate is relatively low. We have shown that this phenomenon is because large-sized silicon nanoparticles in the solution system settle on a top substrate due to their low density during crystallization. It was considered that these processes occur due to the formation of large-sized silicon nanoparticles at high temperatures. Placing large-sized nanoparticles on the substrate located above causes some defects in the formation of single crystals in this part. Experiments have shown that when the distance between the top and bottom Si substrates is less than 1.2 mm, crystal layers of the same thickness can be obtained from the solution on both substrates.
Keywords: Silicon, molecule, nanoparticle, sedimentation.

Introduction

Obtaining Si, Ge, GaAs, ZnSe, and other semiconductor materials, as well as complicated solid solutions based on them from the $A^{IV}B^{IV}$, $A^{III}B^{V}$, and $A^{II}B^{VI}$ classes with the lowest energy consumption and highest crystalline perfection, is a critical challenge in the semiconductor area.

Typically, these materials are produced in large quantities from a high-temperature solution (at the melting point). This consumes much energy and increases the difficulty of forming complicated compound semiconductor solid solutions. Complicated solid solutions ($A^{IV}B^{IV}$, $A^{III}B^{V}$-$A^{II}B^{VI}$, C_2^{IV}-$A^{III}B^{V}$, C_2^{IV}-$A^{II}B^{VI}$, etc.) allow the creation of semiconductor materials and structures with various photoelectric and electrophysical properties. It is possible to create a material or structure with a specified photoelectric and electrophysical property by manipulating the technological process of the growth model (growth temperature, solution-melt composition, cooling rate, orientation, and substrate material, for example). It is also critical to emphasize that the quality, long endurance, and dependability of these materials are dependent on their crystalline perfection. The appropriateness of these materials and structures based on them is determined by growing a single crystal with the lowest dislocation and defect densities. As a result, one of the most significant factors in semiconductor instrumentation is the condition for analysing the ideal regime for generating epitaxial layers of a solid solution and structures (heterostructures).

The work [1] presents simulation models developed for growing semiconductor single crystals by liquid phase epitaxy (LPE). The growth of silicon, binary and ternary systems are shown. Some models developed for epitaxial lateral growth and transformation of semiconductor layers by the LPE method are presented. The influence of gravity on convection is studied in the LPE growth system. Various simulation results are discussed.

Liquid phase growth of silicon at low temperatures has been studied and its application in thin-film solar cells has been presented [2].

A growth technology that enables the growth of Si-Sn epitaxial films under constant temperature conditions by controlling the evaporation of the solvent from a silicon-saturated solution has been investigated. Analytical models designed to predict the evaporation rate of Sn, In and Cu solvents and the crystallization rate of silicon were studied. Crystal growth experiments were carried out to verify the model's accuracy. Thin Si films were grown from Sn-Si and In-Si solutions under a high vacuum at temperatures ranging from 900°C to 1200°C. The predicted solvent evaporation rate and Si growth rate are consistent with experimental measurements [3].

The authors of [4] showed the growth of epitaxial Si layers on Si substrates from pure Si melts using the liquid-phase epitaxy (LPE) method of immersion to exclude the effect of doping with metal solutions on the purity of epitaxial Si layers. They concluded that epitaxial Si layers can be grown on Si substrates from a pure Si melt only if the temperature of the Si growth melt is maintained 1–2°C higher than the Si melting temperature and the growth melt is cooled immediately. But this method is energy-intensive.

Epitaxial layers of Si (single crystal) and polycrystals of Si were identified using the electron backscatter diffraction pattern (EBSP), that is, based on the image of the cross-sections of the films.

A thin layer of Si (d<50 μm) has been experimentally grown on porous silicon by liquid phase epitaxy (LPE). This layer was used as a buffer layer to grow a 50 μm thick epitaxial layer on foreign substrates such as ceramics. The work was carried out stepwise in the following order: forms of porous Si by (100) and (111) with HF anodization on Si wafers, followed by annealing in H_2 atmosphere and Si LPE growth at different temperatures. Porous Si was used as the substrate. The growth of uniform layers on the p-Si (111) wafer was achieved. On the Si (100) surface, growth was observed only in the pyramidal state [5].

A process has been developed for growing thin Si films on inexpensive substrates, with deposition by the method of stationary growth from solution on a reorganized porous silicon foil or a glass substrate with a thin seed layer of amorphous silicon. The corresponding single-crystal and polycrystalline Si films are grown to a thickness of several tens of micrometres, which makes them suitable for efficiently absorbing sunlight into photovoltaic devices. The structural properties of Si films were studied by transmission and scanning electron microscopy [6].

Also, some works [7] show growth by the LPE method for growing single and multilayer GaAs compounds from a dilute solution. As a heterostructure, the growth rate, surface morphology, carrier concentration, and Hall mobility have been investigated. The relationship between supercooling and crystal growth temperature (ΔT) range was studied. Achieved control of the rate of growth.

To avoid the effects of structural supercooling, an attempt was made to maintain the solid-liquid interfaces by growing the epitaxial layer at a constant temperature in the system.

According to the authors, an ideal epilayer and several smooth layers were obtained, although the crystal lattice parameters of Si (a_{Si}=5.43·10^{-10} m) and GaAs (a_{GaAs}=5.66·10^{-10} m) are quite different.

Many studies have been conducted on the growth of Si and $Si_{1-x}Ge_x$ epitaxial layers in Sn solvent. In these studies, it was observed that the number of defects in the crystals formed during the growth of epitaxial layer films from liquid solution onto horizontally placed Si substrates depends on the distance between the substrates [8, 9]. Therefore, it is advisable to take into account the thickness of the substrates in the solution. The fact that epitaxial layer films grown on a top substrate have more defects and are relatively thicker encourages the study of this situation.

Based on the above data, we performed calculations using the sedimentation method. Observations in our experiments showed that when epitaxial layers were grown on Si substrates arranged in the top and bottom positions (horizontally), the epitaxial films on the top substrate grew thicker. Theoretical calculations were performed to describe this phenomenon, and we concluded that crystal-perfect epitaxial layers of Si can be obtained from a limited volume of the Si-Sn solution (depending on the location of the substrates and the distance between them). We assumed that nanoclusters in the solution participate in the formation of crystals.

In the future, this scientific method may allow us to determine the conditions of the optimal growth regime for obtaining complex solid solutions and structures.

Materials and Methods

Chemically pure samples of Sn and Si (Taizhou ATS Optical Material Co., Ltd.) were used for the experiment. Si the plate with <111> orientation was used as substrate.

The experiment was carried out in an EPOS-type device (Pd-15T scavenger) and a 4-channel K-type thermometer was used to probe the temperature in an H_2 atmosphere from 973 K to 1323 K [10]. Si crystals were grown by cooling a Si-Sn solution containing 9.99 at.% Si at a rate of 1 ºC/min starting from a temperature of 1323 K. AE ADAM NBL 214e (Germany) analytical balance was used to measure the weight of the substances.

The thicknesses of the grown Si epitaxial layers were measured using an optical microscope «Optik_B-150 DBR»-USB (Italy), An XRD-6100 Shimadzu (Japan) X-ray diffractometer was used to obtain X-ray diffractograms of the obtained Si crystals. The grown epitaxial layers were studied using a Tescan Vega 3 LMH scanning electron microscope (Czech Republic) with a Bruker XFlash 5010 characteristic X-ray detector.

Results and Discussion

Crystalline perfection of Si epitaxial layers growing from a liquid phase solution of limited volume between horizontal substrates depends on several factors (temperature, distance between substrates placed in a solution of limited volume and their location, cooling rate, solution composition, etc.).

The following conditions were observed in the results, and the differences in the thickness and crystal qualities of epitaxial layers growing on horizontally located substrates (on top of each other) were determined. In cases where the distance between the substrates is up to 1.2 mm, the epitaxial layers grow on the top and bottom substrates with the same thickness. If *d*>1.2 mm, a thicker epitaxial layer was grown compared to the top substrate. We focused on explaining this situation based on the phenomenon of sedimentation and studying the reasons for its origin.

Because Si epitaxial layers are formed from Si molecules (nanoclusters) and large nanoparticles in solution. Due to the low density and low diffusion rate of the large Si nanoparticles compared to the medium, they move towards the substrate located in the top part. As a result, large Si nanoparticles grow more on the substrate located in the top part. Small-sized silicon molecules (nanoclusters) are placed on both substrates in the same amount, and the process of crystal growth takes place. Because the speed of diffusion of small particles is very high. Therefore, the laws of sedimentation do not apply to small particles.

We determine the sizes of silicon molecules or nanoclusters involved in the crystal growth process using Eq. (1) [11].

$$r_c = \frac{2\sigma_{s-l} V_m T_l}{L\Delta T} \tag{1}$$

here, V_m – is the molar volume of the crystal, $\sigma_{s\text{-}l}$ – solid-liquid surface tension (J/m^2), L – heat of fusion (J/mol), ΔT – is the difference between the liquefaction and crystallization temperatures (K).

Table 1 – Sizes of nanoclusters forming silicon crystals at different crystallization temperatures

T_{cr}, K	Nanocluster radius, nm
1323	2.60
1273	2.33
1223	2.10
1173	1.90
1123	1.77
1073	1.65
1023	1.54

In the process of crystal growth from the liquid phase solution to the substrate, the participation of nanoclusters makes a large share. It is important to know the structure, stability and size of the particles involved in the process. However, the experiments showed that large-sized particles also participate in the crystallization process and affect the formation of crystals.

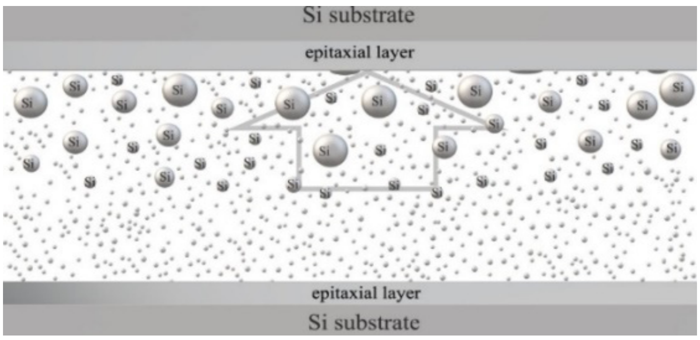

Figure 1 – Schematic of the position of large silicon particles on the top substrate in a finite volume solution (*d*>1.2 mm).

We will analyse the process of growing silicon epitaxial layers from a tin solution of limited-volume silicon and the results obtained from it.

An anomalous condition is observed in the thickness of the crystallizing epitaxial layers on the horizontally placed top substrate (d>1.2 mm) in the limited volume solution (compared to the bottom-placed substrate) (Figure 1). To study this situation, it was determined the size of the large silicon nanoparticles located on the substrates in the top part (at d=2 mm) due to the phenomenon of reverse sedimentation. Eq. (2) was used to determine the size of large silicon nanoparticles [12-14].

$$r_n = \sqrt{\frac{9\eta m'}{2g m_0(\rho_S - \rho_S)t'}} \qquad (2)$$

m_0 – is the mass of large silicon nanoparticles located on the top substrate. The m_0 value was determined from the difference in the masses of the epitaxial silicon layers grown on the top and bottom layers. This mass difference is caused by large silicon nanoparticles. At each time interval, the masses of large silicon nanoparticles on the growing surface were determined from the growth rate of the crystal.

These large-sized silicon nanoparticles participate in the crystallization process and cause the deterioration of the crystal quality of the epitaxial layers growing on the top substrate. As a result, polycrystals can be formed on the substrate (Figure 2). It was observed that relatively crystal-perfect epitaxial layers grow on the bottom substrate (Figure 3).

Table 2 – Sizes of large-size silicon nanoparticles posited on the surface of the substrate

***T*, K**	***t*, min**	***m'*(Si),·10^{-7}, kg**	**r_n(Si), nm**
1323	0	-	-
1273	50	5.88377	69.80
1223	100	10.6665	67.74
1173	150	14.4634	65.58
1123	200	16.8398	62.68
1073	250	19.1677	61.38
1023	300	20.6930	59.92
973	350	21.9486	59.18

An X-ray diffractogram of a film consisting of silicon epitaxial layers grown on a bottom substrate is presented in Figure 3. The resulting X-ray diffractogram contains peaks characteristic of silicon crystal, and the absence of other additional peaks indicates that the film is monocrystalline. Diffractogram Match3! was analyzed in the program. As a result of the analysis, it was found that the size of the unit crystal lattice of silicon is 5.43 nm and the shape is cubic (Fm-3d). These indicators correspond to the indicators of pure silicon crystals reported in the literature.

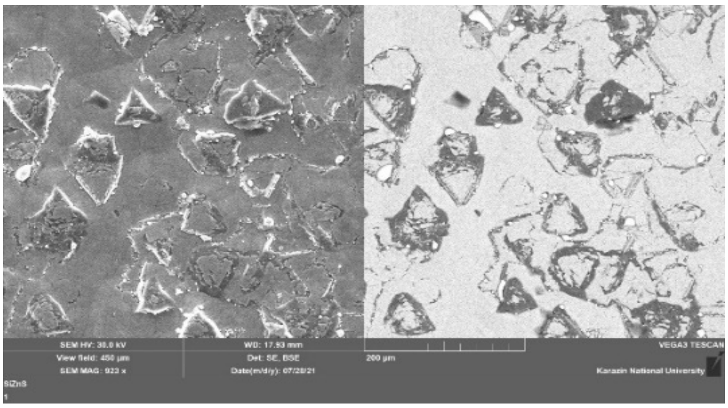

Figure 2 – The formation of a layer of polycrystalline silicon on the top substrate

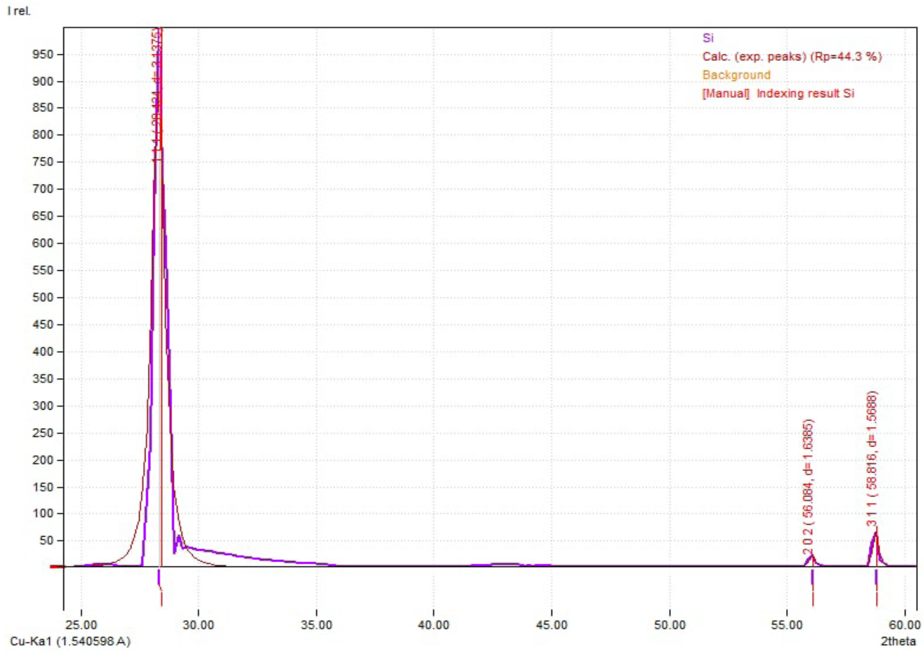

Figure 3 – An X-ray diffractogram of a film consisting of silicon epitaxial layers grown on a bottom substrate

Conclusion

To grow perfectly crystalline epitaxial layers on the top and bottom layers, the distance between the substrates should be $d \leq 1.2$ mm. If $d > 1.2$ mm, the formation of polycrystals can be observed on the top substrate, since large-sized nanoparticles settle on the top horizontal substrate and participate in crystal growth.

Since the density of large-sized Si nanoparticles is small compared to the density of the solution, the probability of settling on the top substrate is high. These theoretical conclusions are consistent with experimental results. The results of this study can be relied on to obtain high-quality epitaxial layers.

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