



Theoretical Evaluation of Silicon Crystal Growth Using Gallium Solvent

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Abstract: Semiconductor materials are of great importance throughout the world. Silicon crystals are this field's most widely used and relatively inexpensive material. Obtaining low-dislocation and defect-free silicon crystals is one of the current issues, and we theoretically investigated the production of low-defect silicon crystals from silicon-gallium melt. We considered the defects that appear in the silicon crystals grown from the solution related to the large-sized silicon nanoclusters involved in the crystal formation based on the obtained results, we showed the conditions for obtaining silicon crystals with few defects from the silicon-gallium solution.

Keywords: Silicon, Defect, Nanocluster, Solution, Gallium.

1. INTRODUCTION

Obtaining semiconductor materials under uniform technological conditions has been of great importance. Since producing semiconductor crystals from liquid solutions is carried out at lower temperatures than other methods, energy consumption is low and environmentally friendly. The liquid phase growth method is promising for obtaining thin epitaxial layers and multilayer structures. However, in most cases, it is observed that the dislocation density is high and there are more defects on the surface of the formed crystals. Many solvent materials have been used to grow Si and Si-containing solid solution semiconductor crystals. To clean Si crystals in production processes, it was studied to obtain silicon crystals from Si-Al solution. However, the results showed that there were defects on the surface of the obtained Si crystals, and it was known that Al was included in the composition [1]. Si crystals were grown from a solution of Si in Na metal at low temperatures. In this case, Na metal in the solution was vaporized at temperatures of 1173 K and below, saturating the solution and obtaining Si single crystals [2]. The main advantage of the solution growth method is that the crystals grow at temperatures below the melting temperature and

the crystal growth occurs spontaneously through nucleation or crystallization. On the other hand, crystal growth in solution is much slower [3]. Due to the small density difference in the Si-Fe solution, it is difficult to separate Si from the solution. In the Si-Cu solution, Cu and Si can form intermediates during directional crystallization, which makes it difficult to remove Cu from Si [4-8]. Therefore, effective solvents that are useful for Si growth rate, benefaction, and purification are in high demand.

It has been studied that the growth of Si crystals using Ga-Si, Au-Si and Ag-Si solutions can prevent the introduction of polluting additives metals such as Ni, Co, Fe and Cr into the crystal structure [9]. Studies on the effect of gallium (Ga) doping on Czochralski (CZ) Si crystal growth have also been carried out. When Ga was directly added to molten Si, only a few clusters of Ga atoms were detected from the surface of the Si solution during crystal growth. It was confirmed that Ga concentration is very small in millimeter measurements made in several steps along the direction of crystal growth [10]. Based on these data, we theoretically investigated the formation mechanisms of Si crystals from Si-Ga melt and the conditions for the formation of low-defect crystals.

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2. THEORETICAL PART

The formation of crystals in the solution is related to the saturation of the solution, in which nanoclusters of crystals (formers of crystal centres) play an important role. The nanoclusters formed in the solution unite and cause crystals to grow. Nanoclusters are very active particles that always tend to reduce their surface free energy. Due to this, the merging of nanoclusters and the formation of large aggregates are observed. Determination of the size of nanoclusters formed in a saturated solution is carried out using the Equation (1) [11, 12]:

$$r_c = \frac{2\sigma_{s-l} \cdot V_m}{\Delta G_V} \quad (1)$$

where V_m - molar volume (m^3), σ_{s-l} - specific surface tension at the liquid-solid interface (J/m^2), ΔG_V - volumetric Gibbs energy (J/mol).

The volumetric Gibbs energy (ΔG_V) of nanoclusters in the solution medium is related to the volumetric dimensions of the particles. If the size of the nanocluster is small, the share of its surface Gibbs energy (ΔG_s) will be larger, and the volume Gibbs energy will have a smaller contribution. As the size of the nanocluster increases, the percentage of volumetric Gibbs energy increases. Volumetric Gibbs energy values are determined using the Equation (2) [11].

$$\Delta G_V = \frac{\Delta H_f \cdot (T_1 - T)}{T_1} \quad (2)$$

where, ΔH_f is the heat of fusion (J/mol), T_1 is the temperature of liquefaction (K), and T is the temperature of nanocluster formation (K).

It is important to determine the ratio of concentrations of nanoclusters formed at temperature T in the solution environment to large-sized particles. The higher the concentration of nanoclusters in the medium, the less defective the crystal formed from their fusion is. The ratio of the concentrations of particles in the environment of the concentrations of large particles is determined by Equation (3) [12].

$$r = \frac{2\sigma_{s-l} V_m}{RT \ln \frac{C_r}{C_\infty}} \quad (3)$$

In the equation, R is the universal gas constant ($8.314 J \cdot K^{-1} \cdot mol^{-1}$), r is the radius of the nanocluster

(m), C_r is the concentration of nanoclusters with radius r , and C_∞ is the concentration of large-sized particles.

The process of crystallization from a solution and the processes of melting (mixing of solution components) are interdependent. As mentioned above, nanoclusters are directly involved in the crystallization process, and it is important to know the Gibbs energies of their formation. The interdependence between the maximum Gibbs energy of formation ($\Delta G_{max,cr}$) and the Gibbs energy of mixing (ΔG_{mix}) of nanoclusters in the medium determines the Gibbs energy of this system. The highlighted parameters are determined as follows [13, 14].

$$\Delta G_{mix} = RT(X_1 \ln X_1 + X_2 \ln X_2) \quad (4)$$

$$\Delta S_{mix} = -R(X_1 \ln X_1 + X_2 \ln X_2) \quad (5)$$

$$\Delta G_{max,cr} = \frac{16\pi\sigma_{s-l}^3 V_m^2}{3\Delta G_V^2} \quad (6)$$

$$\Delta G_{system} = \Delta G_{max,cr} + \Delta G_{mix,then} - \Delta G_{mix,first} \quad (7)$$

where, ΔG_{mix} - mixing Gibbs energy (J/mol), ΔS_{mix} - entropy of mixing ($J \cdot mol^{-1} \cdot K^{-1}$) X -mol fraction, $\Delta G_{max,cr}$ - maximum formation Gibbs energy (J/mol).

The temperature at which the change in the Gibbs energy of the system is the smallest can be considered the energetically optimal temperature of the crystallization process. Carrying out the process under conditions with a lower value of Gibbs energy results in the least consumption of energy. Therefore, it is important to determine the Gibbs energy of the system. The size of the defects that can be formed on the surface of the crystals forming in the solution determines the quality of the crystal. Equation (8) can be used to determine defect sizes (b) on the crystal surface [12].

$$\Delta G_{max,cr} = \frac{4\sigma_{s-l} b V_m}{\Delta G_V} \quad (8)$$

Using the above information, we can determine the conditions for growing crystals with few dislocations and few defects from the solution.

3. RESULTS AND DISCUSSION

Since the solubility of silicon (Si) in gallium (Ga) is very good, it is important to grow Si and Si-containing crystals from this solution. It should also be noted that Ga does not contaminate growing Si crystals. In our previous papers, we have published information about the participation and importance of nanoclusters in the medium in crystal growth from solutions [15, 16]. The defect-free surface of the crystals growing from the solution is also related to the amount of nanoclusters of the same size participating in the process. Therefore, it is important to determine the sizes and quantitative indicators of nanoclusters involved in the crystallization process. We determined the radius of the nanoclusters involved in the crystallization process at temperatures of 873-1273 K (Figure 1).

In the growth of a Si crystal from a solution of Si in Ga, the difference in the size of the nanoclusters in the solution causes defects on the surface of the crystal. The presence of nanoclusters in the crystal growth, and the fact that they are the same and smaller in size, or that there are few differences between their sizes, creates the possibility of obtaining a crystal with fewer defects.

At higher temperatures, the sizes of Si nanoclusters become larger. Large-sized nanoclusters lead to an increase in defects in the growing crystal. Therefore, we considered the maximum temperature to study the crystallization process to be 1273 K. We determined the changes in the sizes of Si nanoclusters formed in the solution of Si in Ga depending on different temperatures. Depending on the temperature, the size of Si nanoclusters in the solution corresponded

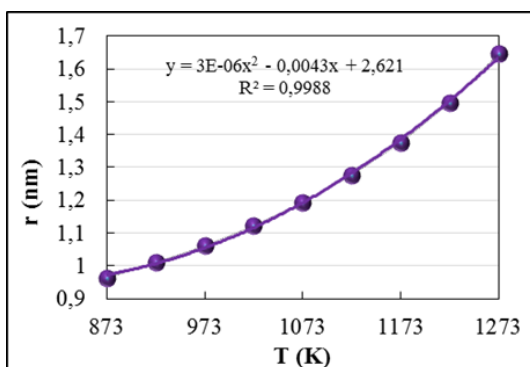


Fig. 1. Temperature dependence of the sizes of Si nanoclusters in the Si-Ga solution.

to the appearance of a polynomial function. At temperatures below 1073 K, the difference between the sizes of Si nanoclusters was observed to be small. In studies, we have published the results of experiments determining the sizes of Si and Ge nanoclusters dissolved in Sn solvent. In these studies, we showed that the size of Si and Ge nanoclusters decreased with a decrease in temperature [15, 17]. If Si crystals are grown from a Ga-Si solution starting from a temperature of 1073 K, the probability of obtaining perfectly crystalline films is high. We used the activity parameters used for real processes to explain the crystallization process in the Si-Ga solution more precisely. It will be possible to obtain results closer to real systems through the activity (a) parameters of the components in the solution. For this purpose, we determined and used the activities of Si and Ga components [18] based on the literature.

When considering the processes of crystallization in solutions, it is important to determine the Gibbs energy of mixing (ΔG_{mix}). To determine the Gibbs energy of mixing for real systems, we use the following equation [19]:

$$\Delta G_{\text{mix}} = RT(X_{\text{Si}} \ln a_{\text{Si}} + X_{\text{Ga}} \ln a_{\text{Ga}}) \quad (9)$$

where, X_{Si} and X_{Ga} are the mole fractions of silicon and gallium, and a_{Si} and a_{Ga} are their activities.

Using Equation (9), the Gibbs energies of mixing for a real solution of Si-Ga were calculated. In the process of cooling the Si-Ga solution, it was found that the Gibbs energy of mixing of the system increases in a curved form depending on the temperature (Figure 2).

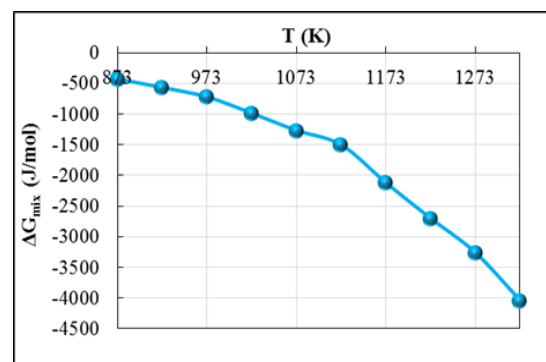


Fig. 2. Temperature dependence of the Gibbs energy of mixing of Si and Ga.

The increase in the Gibbs energy of mixing at lower temperatures causes a decrease in the solubility property in this situation. In such cases, the solute is more likely to separate from the solution by forming crystals. When the entropy of mixing (ΔS_{mix}) change of the components in the solution was studied, the value of ΔS_{mix} decreased with decreasing temperature (Figure 3). Decreasing the value of ΔS_{mix} means reducing the disorder level of components in the system. In such a situation, the probability of the transition of particles from disorder states to order states increases.

$$\Delta S_{\text{mix}} = -R(X_{\text{Si}} \ln a_{\text{Si}} + X_{\text{Ga}} \ln a_{\text{Ga}}) \quad (10)$$

By determining the Gibbs energies of the maximum formation of Si nanoclusters in the solution, it is possible to determine the results of the total Gibbs energy of the process system (ΔG_{sis}). We used Equation (6) to determine the Gibbs energy of the maximum formation of nanoclusters. Based on the obtained results, a temperature dependence graph of maximum Gibbs energy of Si nanoclusters

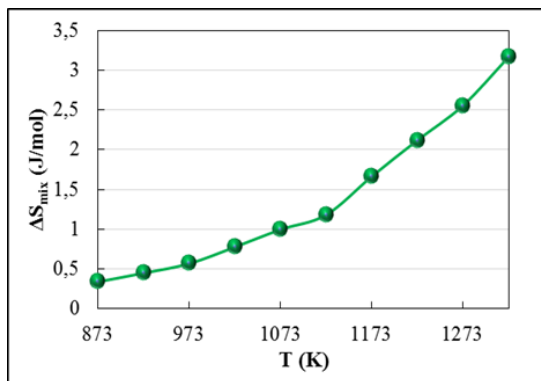


Fig. 3. Temperature dependence of the entropy change of mixing Si and Ga.

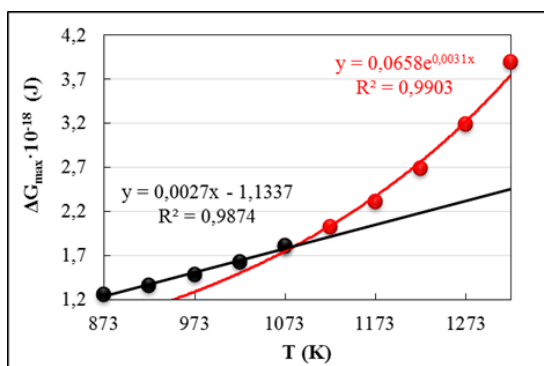


Fig. 4. Temperature dependence of maximum Gibbs energies of Si nanoclusters.

formed in Ga medium was drawn and attention was paid to the changes. Changes in the graph showed that the Gibbs energy changes exponentially from 1273 K to 1073 K as the temperature decreases. As the temperature decreases from 1073 K to 873 K, a linear change of Gibbs energy is observed (Figure 4). The change in the Gibbs energy of the solution system was found by subtracting the differences between the initial and final values of the Gibbs energies of mixing from the maximum Gibbs energy of the nanoclusters causing crystallization (Equation (7)).

In the process of growing Si crystals from the Si-Ga solution, the temperature dependence graph of the Gibbs energy of the system can be divided into 2 parts. In the temperature range of 873-1073 K, it was observed that the change of Gibbs energy of the system is linearly dependent on temperature, and at temperatures of 1073-1273 K, it is exponential (Figure 5). During the growth of Si from the solution, the temperatures in the states of linear variation of the Gibbs energy of the system are important. Because the Gibbs energy of the system changes linearly (depending on the temperature), the energy differences at each process stage are smaller.

Using the results obtained above, the ratio of the concentration of nanoclusters in the Si-Ga solution to the concentration of large particles was determined (using Equation (3)). It was found that the concentration of Si nanoclusters with the radius r in the solution increases with the decrease in temperature (Figure 6). This means that at low temperatures, the concentration of nanoclusters is greater than that of large-sized particles.

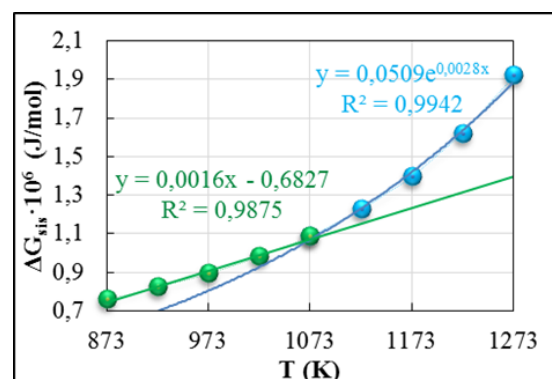


Fig. 5. Gibbs energy change of the system during the growth of Si crystals from Si-Ga solution.

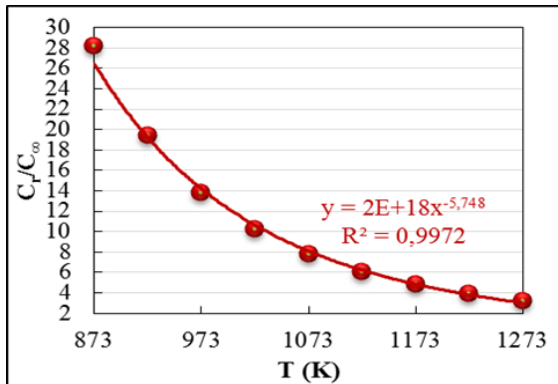


Fig. 6. The ratio of the concentrations of Si nanoclusters at different temperatures to the concentrations of large particles in the solution.

If we pay attention to all the determined results, it can be seen that as the temperature decreases, the size of Si nanoclusters in the solution decreases and their concentration increases. This situation can allow obtaining Si crystals with fewer defects (less dislocations) from the Si-Ga solution. Dislocations that appear on the surface of the crystal are related to defects on the surface.

Studying the sizes of initial 2D defects that appear on its surface during crystal growth helps to determine the conditions under which crystals with fewer defects can be obtained. The size of the defects formed on the surface of the Si crystal growing from the Si-Ga solution is depicted in the temperature dependence graph (Figure 7). The sizes of these defects are determined using Equation (8).

If we pay attention to the results, it can be seen that the sizes of 2D defects formed on the surface of Si crystals growing in Si-Ga solution are small. The size of the defect was around 1 nm at 1323 K and at temperatures below 1273 K, the size of nanoclusters decreased sharply below 1 nm. These indicators show that obtaining Si and Si-containing crystals in Ga solvent is possible with few dislocations and defects.

4. CONCLUSIONS

The possibilities of growing Si crystals from liquid Si-Ga solution were considered. The results of the study showed that the size of the nanoclusters involved in the crystallization process becomes relatively small with the decrease in temperature, and the defects on the surface of the crystals growing from this solution are very likely to be very small.

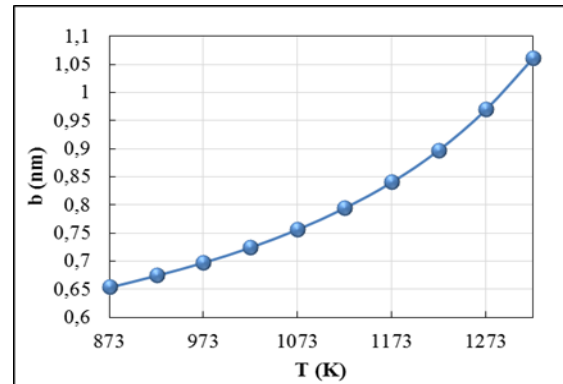


Fig. 7. 2D dimensions that can be formed on the surface of Si crystals growing from a Si-Ga solution.

It was found that the concentration of nanoclusters increases as the temperature decreases. Based on these results, it can be concluded that the use of Ga solvent is very promising for obtaining crystals with low dislocation density and few defects and semiconductor structures based on them.

5. CONFLICT OF INTEREST

The authors declare no conflict of interest.

6. REFERENCES

1. Y. Nishi, Y. Kang, and K. Morita. Control of Si crystal growth during solidification of Si-Al melt. *Materials Transactions* 51(7): 1227-1230 (2010).
2. H. Morito. Low-temperature synthesis of Si and Si-based compounds using Na. *Journal of the Ceramic Society of Japan* 122(1432): 971-975 (2014).
3. I. Milisavljevic and Y. Wu. Current status of solid-state single crystal growth. *BMC Materials* 2: 2 (2020).
4. G. Qian, L. Zhou, S. Li, Z. Wang, and L. Sun. Enhanced In Situ Separation of Boron at the Silicon Alloy Solidification Interface through Innovating the Impurity Chemical Reconstruction Approach for SoG-Si. *ACS Sustainable Chemistry & Engineering* 9(33): 11179-11193 (2021).
5. G. Qian, L. Sun, H. Chen, Z. Wang, K. Wei, and W. Ma. Enhancing impurities removal from Si by controlling crystal growth in directional solidification refining with Al-Si alloy. *Journal of Alloys and Compounds* 820: 153300 (2020).
6. L. Sun, Z. Wang, H. Chen, D. Wang, and G. Qian. Removal of phosphorus in silicon by the formation of CaAl₂Si₂ phase at the solidification interface. *Metallurgical and Materials Transactions B* 48:

- 420-428 (2017).
7. L. Hu, Z. Wang, X. Gong, Z. Guo, and H. Zhang. Impurities removal from metallurgical-grade silicon by combined Sn-Si and Al-Si refining processes. *Metallurgical and Materials Transactions B* 44: 828-836 (2013).
 8. L. Hu, Z. Wang, X. Gong, Z. Guo, and H. Zhang. Purification of metallurgical-grade silicon by Sn-Si refining system with calcium addition. *Separation and Purification Technology* 118: 699-703 (2013).
 9. E.A. Good, T.H. Wang, T.F. Ciszek, R.H. Frost, M.R. Page, and M.D. Landry. Partitioning effects in recrystallization of silicon from silicon-metal solutions. In *12th Workshop on Crystalline Silicon Solar Cell Materials and Processes, Breckenridge, Colorado* (2002).
 10. T. Hoshikawa, T. Taishi, S. Oishi, and K. Hoshikawa. Investigation of methods for doping CZ silicon with gallium. *Journal of Crystal Growth* 275(1-2): e2141-e2145 (2005).
 11. P. Rudolph. Thermodynamic Fundamentals of Phase Transitions Applied to Crystal Growth Processes. In: *Crystal growth Technology*. H.J. Scheel and T. Fukuda (Eds.). *John Wiley & Sons, New York* pp. 15-42 (2003).
 12. E.D. Shchukin, A.V. Pertsov, E.A. Amelina, and A.S. Zelenev (Eds.). *Colloid and Surface Chemistry. Elsevier Science* (2001).
 13. D.R. Gaskell and D.E. Laughlin (Eds.). *Introduction to the Thermodynamics of Materials*. 6th Edition. *CRC Press, Boca Raton* (2017).
 14. A.D. Pelton (Ed.). *Phase Diagrams and Thermodynamic Modeling of Solutions*. *Elsevier, München* (2019).
 15. A. Razzokov, and K. Eshchanov. Thermodynamic Bases for Obtaining Crystalline Perfect Silicon from Tin-silicon Solution. *International Journal of Thermodynamics* 25(2): 1-6 (2022).
 16. A. Razzokov and K. Eshchanov. Optimal Regime for Growth of Epitaxial Germanium Layers from the Liquid Phase Based on Thermodynamic Calculations. *International Journal of Thermodynamics* 25(3): 41-45 (2022).
 17. A.S. Razzokov, A.S. Saidov, V.V. Girzhon, and O.V. Smolyakov. Features of growing Si- and Si_{1-x}Ge_x-single-crystal films from solution-melt based on tin. *Journal of Physical Studies* 26(4): 4601-4605 (2022).
 18. J. Safarian, L. Kolbeinsen, and M. Tangstad. Thermodynamic activities in silicon binary melts. *Journal of Materials Science* 47: 5561-5580 (2012).
 19. P.W. Atkins and J. de Paula (Eds.). *Atkins' Physical Chemistry*. Eighth Edition. *W.H. Freeman and Company, New York* (2006).