Automated Growth of Si$_{1-x}$Ge$_x$ Single Crystals with Constant Axial Gradient by Czochralski Technique

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1. Introduction

Si-rich Si$_{1-x}$Ge$_x$ gradient crystals can be used as monochromator for X-ray or γ-ray diffraction in both, Bragg (reflection diffraction) and Laue (transmission diffraction) geometry. In the first case, the lateral change of the spacing between the crystalline planes with rising Ge content along the crystal can be used for the monochromatization of a divergent incident beam. Thus, the variation of the Bragg angle of divergent beams along the monochromator can be compensated. It was realized in the SiGe (220) double crystal monochromator at the BESSY II KMC-2 beamline. The spectral flux density in this case was found to be 4–6 times higher than for Si monochromator due to optimization of the Bragg conditions. At the same time an energy resolution smaller according to the equation obtained from Scheil–Pfann model-based control methods.

All Czochralski (CZ) grown Si$_{1-x}$Ge$_x$ crystals are gradient crystals because of the segregation of the components. The axial Ge distribution is non-uniform and corresponds to the well-known Scheil–Pfann equation. It means that the gradient of Ge changes over the crystal length, too, and the curvature of diffracting planes increases continuously. It is not practicable for their application as monochromators because the diffracting conditions will be changing from one point to another along the crystal axis.

The method for the growth of Si-rich Si$_{1-x}$Ge$_x$ single crystals with the constant gradient of Ge was first described in ref. [7]. Such crystals can be grown when the diameter of the crystal gets smaller according to the equation obtained from Scheil–Pfann under the condition of a linear distribution of the second component (Ge in our case). The method of computation of the required crystal diameter proposed in ref. [7] does not consider all aspects of the special nature of the SiGe-system, especially the continuously changing densities of the solid and the liquid phase at the interface. This will be addressed in this work. Furthermore, in order to grow crystals with a constant gradient of Ge one needs to precisely control the crystal diameter in dependence on the crystal length. For this purpose an automated diameter control system is desired. This paper describes the automated CZ growth of Si$_{1-x}$Ge$_x$ single crystals with constant axial gradient of Ge using model-based control methods.

2. Growth Concept

In this section the necessary steps for the computation of the crystal radius reference trajectory are presented according to the conventional approach. It will be shown that this approach is not sufficient to achieve a constant concentration gradient on the required level and an alternative is proposed.

2.1. Basic Mathematical Model

Let $C_{Ge}$ denote the initial concentration of Ge in the solid phase. Then, the concentration $C_{Ge}$ of Ge at crystal length $l$ reads...
theresult into Equation (3) one obtains

\[
C_{0,Ge}^i = C_{0,Ge}^i \cdot (1 - g(l))^{k-1}
\]

(1)

where \( k \) is the distribution coefficient and \( g \) the mass ratio

\[
g(l) = \frac{m_i(l)}{M_0}
\]

(2)

with the crystal mass \( m_i \) and the initial melt mass \( M_0 \). It is assumed that \( C_{0,Ge}^i = k \cdot C_{0,Ge} \) with the initial concentration \( C_{0,Ge}^i \) of Ge in the melt. Typical values of \( C_{0,Ge}^i \) used in this work are 5 or 7 at%. It means that \( x = 0.05 \) or 0.07 in Si_{5-7}Ge_c.

During growth the constant gradient condition can be formulated as

\[
\frac{\partial C_{0,Ge}^i}{\partial l} = B = \text{const.}
\]

(3)

By differentiating Equation (1) with respect to \( l \) and inserting the result into Equation (3) one obtains

\[
\frac{\partial C_{0,Ge}^i}{\partial l} = -\frac{C_{0,Ge}^i}{M_0} \cdot (k - 1) \cdot \left(1 - \frac{m_i(l)}{M_0}\right)^{k-2} \cdot m'_i(l) = B
\]

(4)

with

\[
m'_i(l) = \pi \rho'(l) \cdot r_i(l)
\]

(5)

which results from

\[
m_i(l) = \pi \int_0^l \rho'(\lambda) \cdot r_i(\lambda) \, d\lambda.
\]

(6)

In the last two equations \( \rho' \) denotes the density of the solid phase and \( r_i \) denotes the crystal radius at the solid–liquid interface. For the density the following holds:

\[
\rho'(l) = (1 - x(l)) \cdot \rho'_{0,\text{Si}} + x(l) \cdot \rho'_{0,\text{Ge}}
\]

(7)

with the nominal densities \( \rho'_{0,\text{Si}} \) and \( \rho'_{0,\text{Ge}} \) of Si and Ge, respectively, and the Ge fraction \( x \) in the crystal. For this, one has according to Equation (1):

\[
x(l) = x_0 \cdot (1 - g(l))^{k-1} = x_0 \cdot \left(1 - \frac{m_i(l)}{M_0}\right)^{k-1}.
\]

(8)

### 2.2. Approximative Solution

If one assumes that the density \( \rho' \) is constant during the process with the value \( \bar{\rho}' \) (i.e., neglecting the dependency shown in Equation (7)) it is possible to derive a simple analytical solution for the required radius trajectory. Because of the constant gradient, one derives from Equation (3):

\[
C_{0,Ge}^i(l) = B \cdot l + C_{0,Ge}^i.
\]

(9)

### Table 1. Parameter used for radius profile calculation.

| Parameter                        | Value   |
|----------------------------------|---------|
| Nominal density of Si (solid)    | 2330 kg m^{-3} |
| Nominal density of Ge (solid)    | 5360 kg m^{-3} |
| Distribution coefficient of Ge   | 0.32    |
| Payload                          | \( M_0 \) |
| Concentration gradient of Ge     | 0.16 at % cm^{-1} |
| Initial fraction of Ge in melt   | 0.05    |

Inserting Equation (1) and solving for \( m_i \) leads to

\[
m_i(l) = \left(1 - \left(\frac{B}{C_{0,Ge}^i} \cdot l + 1\right)^\frac{1}{k}\right) \cdot M_0.
\]

(10)

After differentiating this equation with respect to \( l \) inserting it into Equation (5) and solving for \( r_i \) one obtains (see also ref. [7]):

\[
r_i(l) = \sqrt{\frac{M_0 \cdot B}{\pi \cdot \bar{\rho}' \cdot (1 - k) \cdot C_{0,Ge}^i \left(\frac{B}{C_{0,Ge}^i} \cdot l + 1\right)^\frac{1}{k+1}}}. \]

(11)

### 2.3. Numerical Solution

An “exact” solution requires the consideration of the variable density \( \rho' \). In that case, Equations (1)–(8) can only be solved numerically w.r.t. \( r_i \) for a given, constant concentration gradient \( B \). To do so one discretizes the total length \( L \) of the crystal in intervals of length \( \Delta l \). Given the required concentration gradient \( B \) in the \( j \)th integration step of Equation (4) one obtains

\[
\frac{C_{0,Ge}^i}{M_0} \cdot (k - 1) \cdot \left(1 - \frac{m_j}{M_0}\right)^{k-2} \cdot \pi \cdot \rho' \cdot j \cdot r_i^2 \cdot j + B = 0
\]

(12)

which has to be numerically solved for \( r_i[j] \) with

\[
m_j = m_j[j - 1] + 0.5 \cdot \pi \cdot \left(\rho' j[j - 1] \cdot r_i^2[j - 1] + \rho' \cdot j \cdot r_i^2 \cdot j \right) \cdot \Delta l
\]

\[
x[j] = x_0 \cdot \left(1 - \frac{m_j}{M_0}\right)^{k-1}
\]

\[
\rho' \cdot j = (1 - x[j]) \cdot \rho'_{0,\text{Si}} + x[j] \cdot \rho'_{0,\text{Ge}}.
\]

Here the trapezoidal approximation has been used for calculating the integral (6).

### 2.4. Comparison of the Analytic and Numerical Solution

For a given concentration gradient of \( B = 0.16 \) at % cm\(^{-1}\) a radius profile has been calculated using the approaches presented in Sections 2.2 and 2.3. The data shown in Table 1 has been used and the results are found in Figure 1.
Figure 1. Calculated radius profile using the approximate analytical solution according to Equation (11) and the exact numerical solution according to Section 2.3. Parameter according to Table 1.

Figure 2. Calculated concentration gradient based on the analytically and the numerically calculated radius profile shown in Figure 1. The difference between the analytically and the numerically calculated profile seems to be negligible. However, if one re-computes the real concentration gradient from the profiles using Equations (4), (6), and (7) one obtains the results presented in Figure 2. It can be clearly seen that the concentration gradient degrades with the growing crystal.

2.5. Realizable Crystal Radius Profile

Another more important question is how to realize the growth of a crystal with a radius profile as shown in Figure 1. It is evident that this is not possible in practice due to the seeding procedure. Usually, an approach as shown in Figure 3 is used. After seeding, the crystal radius is increased until its real trajectory intersects the computed radius reference curve. Then, the radius is tracked along the reference curve. When re-computing the concentration gradient obtained from such a crystal radius profile one obtains the results shown in Figure 4. The figure clearly reveals that the desired concentration gradient of 0.16 at% cm⁻¹ is completely missed throughout the whole process. Hence, it is desirable to find an approach which (a) generates a realizable radius trajectory and (b) ensures that the concentration gradient is kept on its constant reference value.

3. An Alternative Approach

The basic idea to overcome the missed concentration gradient by the method shown in Section 2.5 is to rethink the method of finding the point at which to switch over to the correct crystal radius trajectory. In the approach described in Section 2.5 this is done by just waiting until the crystal is grown to a certain radius and then it is grown along the calculated ideal profile. However, in order to match the system Equations (1)–(8) under a given concentration gradient also the mass ratio (2) has to be correct at the switching point. Hence, a switch over to the ideal crystal radius
Figure 5. Crystal radius reference trajectory calculated according to the method described in Section 3 such that the mass ratio matches that of the ideal curve at the switching point. The cone part of the trajectory, until the radius reaches the ideal radius curve, is described by a simple spline approximation to obtain a smooth crystal shoulder, see ref. [9].

Figure 6. Resulting concentration gradient when using the crystal radius reference trajectory from Figure 5. The usable part of the crystal with the desired constant concentration gradient starts at an approx. crystal length of 43 mm.

The growth of Si-rich Si_{1-x}Ge_x gradient crystals has been carried out in Ar atmosphere under 40 mbar pressure and a gas flow of 600 Nl h^{-1} using the modified CZ technique described in ref. [6]. Because of the Ge segregation there is the danger of constitutional supercooling on the solid–liquid interface leading to a polycrystalline growth. To avoid the loss of the crystallinity, the growth rate should not be higher than the critical growth rate determined by the Tiller criterion. In the case of the Si_{1-x}Ge_x crystal growth from the melt with 5 at% Ge an initial pulling rate of 9 mm h^{-1} was chosen and it was continuously changed in the interval from $g = 0.1$ to $g = 0.9$ to a pulling rate of 3.5 mm h^{-1} because of the increasing of Ge concentration in the melt during the growth.

The automated growth has been performed using the nonlinear model based control system described in ref. [9] comprising of a nonlinear model based controller manipulating the heater power and a state observer for the reconstruction of the crystal radius from the weight measurement.

Figure 7 shows one of the crystals with a gradient of about 0.10 at% cm^{-1} grown from a melt with 5 at% Ge and an initial ingot of 850 g. Crystal orientation is $<111>$. After finishing the conus part of the crystal its diameter has been continuously decreased from 62 to 38 mm according to the calculated radius trajectory. To save the crucible and the graphite susceptor the crystal diameter has been finally increased again to minimize the remaining melt volume in the crucible. The total weight of the crystal is 675 g.

The Ge distribution along the crystal length has been measured by the energy-dispersive X-ray spectroscopy (EDX) method on the longitudinal cut through the middle of the crystal. The results are shown in the Figure 8. The first 40 mm of the crystal corresponds to the conical part of the crystal. The Ge distribution in the main part of the crystal is approximated by the dashed line and shows good linearity with a concentration gradient of 0.108 at% cm^{-1}. This is in good agreement with the desired gradient of 0.10 at% cm^{-1}. The Ge distribution in the thick end part of the crystal is not shown. The micro fluctuations of the Ge concentration could be caused by the crystal diameter fluctuations but they do not influence the macro gradient that is more important for X-ray or γ-ray monochromator applications. The radial distribution of Ge depends on the crystal diameter because it is influenced by the form of the solid–liquid interface. The maximal deviation of the Ge concentration along the crystal diameter from the average does not exceed 0.02 at% and also does not have a noticeable influence on the macro gradient along the crystal axis.
More detailed information about the diffraction properties of the Si-rich Si$_{1-x}$Ge$_x$ gradient crystals is shown in ref. [3].

5. Conclusion

A new approach for the growth of Si$_{1-x}$Ge$_x$ single crystals with constant gradient of composition has been developed using an advanced method for the calculation of the crystal radius reference trajectory and automated control of the crystal radius during the growth process. It has been shown that it is important to take into account all physical effects for the calculation and to ensure that the technical realizable trajectory properly matches the calculated one after the cone phase. The capability of the approach has been successfully shown by experimental verification.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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[1] A. Erko, F. Schäfers, W. Gudat, N. V. Abrosimov, S. N. Rossolenko, V. Alex, S. Groth, W. Schröder, Nucl. Instrum. Methods Phys. Res. 1996, A374, 408.
[2] S. Keitel, C. C. Retsch, T. Niemöller, J. R. Schneider, N. V. Abrosimov, S. N. Rossolenko, H. Riemann, Nucl. Instrum. Methods Phys. Res. 1998, A 414, 427.
[3] N. Barriere, J. Rousselle, P. von Ballmoos, N. V. Abrosimov, P. Courtois, P. Bastie, T. Camus, M. Jentschel, V. N. Kurov, L. Natalucci, G. Roulil, N. F. Brejnholtg, D. Serreh, J. Appl. Crystalogr. 2009, 42, 834.
[4] A. Erko, N. V. Abrosimov, V. Alex, Cryst. Res. Technol. 2002, 37, 685.
[5] R. Smither, K. Abu Saleem, M. Beno, C. Kurtz, A. Khounsary, N. Abrosimov, Rev. Sci. Instrum. 2005, 76, 123107.
[6] N. V. Abrosimov, S. N. Rossolenko, V. Alex, A. Gerhardt, W. Schröder, J. Cryst. Growth 1996, 166, 657.
[7] N. V. Abrosimov, A. I. Erko, V. N. Kurov, S. N. Rossolenko, I. G. Rasin, H. Riemann, Bull. Russ. Acad. Sci.: Phys. 2004, 68, 955.
[8] J. P. Dismukes, W. M. Yim, Trans. Metall. Soc. AIME 1965, 233, 672.
[9] J. Winkler, M. Neubert, J. Rudolph, J. Cryst. Growth 2010, 312, 1005.