Bulletin of the Russian Academy of Sciences
Physics

Vol. 68, No. 6, pp. 955–959
2004

CONTROL OF DISTRIBUTION PROFILE OF COMPONENTS DURING GROWTH OF Si:Ge SINGLE CRYSTALS BY CZOCHRALSKI METHOD

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We showed the possibility to grow gradient crystals based on the Si-rich Si:Ge solid solutions using segregation of the minor component (Ge). We implemented two versions to control the Ge distribution in the length of the $Si_{1-x}Ge_x$ crystal grown from the melt by the Czochralski method due to the choice of the crystal size and shape.

PACS: 81.05.Cy; 81.10.Aj, Fq

1. Introduction

The Si:Ge solid solutions are a promising material for microelectronics and optoelectronics. The Si:Ge thin films are most widely used, while bulk crystals are used mainly for fundamental investigations because of the complexity of their fabrication and high cost [1–5].

Currently, the new field of application of bulk Si:Ge single crystals is X-ray, gamma, and neutron optics. Particularly, high-quality crystals are used in monochromators. As a rule, crystals of the silicon- and germanium-rich sides of the ($Si_{1-x}Ge_x$) phase diagram are used to monochromate X-rays and harder gamma and neutron radiation, respectively. Graded crystals, in which the component concentration varies monotonically over the crystal length, are of the most interest. Due to this variation, the lattice parameter varies monotonically according to Vegard's law. For example, the choice of the gradient for use of the $Si_{1-x}Ge_x$ crystal to monochromate synchrotron radiation allows one to compensate for the divergence of the incident beam thus providing the fulfillment of the Bragg reflection condition for the same radiation wavelength over the whole monochromator surface, which multiply increases the radiation flux at a high degree of monochromaticity [6, 7].

In this work, we report the growth of $Si_{1-x}Ge_x$ graded crystals from the melt by the Czochralski method. The main goal of the investigation was to attain a constant gradient of germanium from 0.7 to 1.0 at.%·cm^{-1} over a crystal length of 8 cm. The value of the gradient and crystal sizes were determined from the parameters of monochromators necessary to equip two emission lines at the Berlin Synchrotron Radiation Source (BESSY).

2. Growth of graded crystals

The $Si_{1-x}Ge_x$ crystals were grown by the Czochralski method using a setup with a resistive heater equipped with an automated system to control the crystal diameter using a weight sensor. The growth procedure was described in detail in [8]. The PC-based control program, in addition to a PID controller which keeps the specified profile (diameter) of the crystal, included a set of functions which allowed us to vary programmably the pulling rate, the rate of rotation of the crucible and crystal, and other growth parameters depending on the crystal weight or the crystallized charge fraction.

The main difficulties in growth of the crystals of the Si:Ge solid solution from the melt are associated with the danger of the appearance of concentration supercooling at the crystallization front. Supercooling is caused by the segregation of the second component, which usually leads to the suppression of the single-crystal growth. To select the growth parameters (most often it is the pulling rate for the growth of the crystal with the specified concentration of components) the Tiller criterion is usually used [9]. This criterion provides an estimate of the highest allowed growth rate at which no concentration supercooling is yet observed. The pulling rate which was estimated according to this criterion for the growth from the melt with 2 at.% Ge was 15 mm·h^{-1}, and for the growth from the melt with 7 at.% Ge it was 6 mm·h^{-1}. To optimize the growth process, we gradually decreased the pulling rate when growing the graded crystal as the Ge concentration increased so as the pulling rate was below the critical rate determined from the Tiller criterion.

There are various variants of control of the crystal composition during the growth. These are a passive control, when the components are naturally redistributed due to segregation, and an active control, when the melt is replenished by one of the components. We actively controlled growth of crystals of the germanium-rich side of the phase diagram [10]. In this case, we used melt replenishment with silicon in order to compensate its loss in the melt during growth since the distribution coefficient of Si in germanium $k > 1$. Silicon was introduced into the melt by dissolving the calibrated Si rods arranged over the crucible perimeter.

Hereinafter, we deal with the passive control of the composition profile during the growth of crystals of the silicon-rich side of the Si:Ge phase diagram. In this case, the gradient is controllable due to the variation in the size and shape of the growing crystal.

3. Growth of cylindrical crystals

The distribution of the germanium concentration C_{Ge} during growth of the $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ crystals by the Czochralski method is described well by the expression [8]

$$C_{\mathrm{Ge}} = kC_{0,\mathrm{Ge}}(1-g)^{k-1}, \tag{1}$$

where k is the distribution coefficient of Ge in Si, which usually depends on the concentration of components, in this work we used for estimations $k = 0.32$; $C_{0,\mathrm{Ge}}$ is the initial concentration of Ge in the melt; and g is the crystallized fraction of the initial melt $(0 < g < 1)$. In the first half of the crystal, the Ge concentration over the length varies weakly and an almost constant gradient is observed, while at $g > 0.6$, the Ge concentration and its gradient noticeably increase as g increases.

Since we grow real crystals, it is more convenient to present g in their cylindrical part as

$$g = M_{\mathrm{cr}}/M_0 = \pi\rho_{\mathrm{cr}}R^2L/M_0, \tag{2}$$

where M_0 is the weight of the initial charge, M_{cr} and ρ_{cr} are the weight and density of the crystal, and R and L are the radius and length of the crystal, respectively. One can see from expressions (1) and (2) that at the constant weight

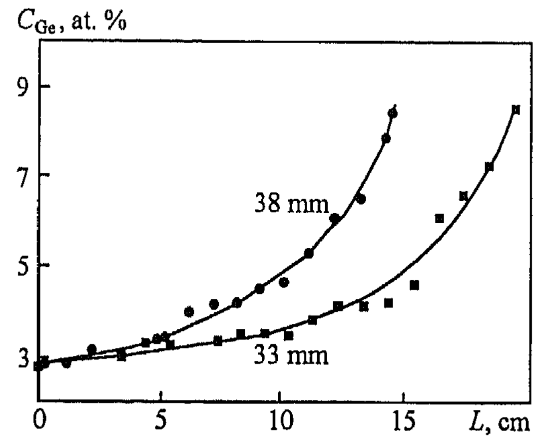

Figure 1. Distribution of Ge in the length of two $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ crystals of diameters 33 and 38 mm, which were grown from the melt at the same initial charge and Ge concentration of 7 at.%. The Ge concentration was determined from the shift of position of the optical phonon (TO) in the IR transmission spectra near the fundamental adsorption edge [11].

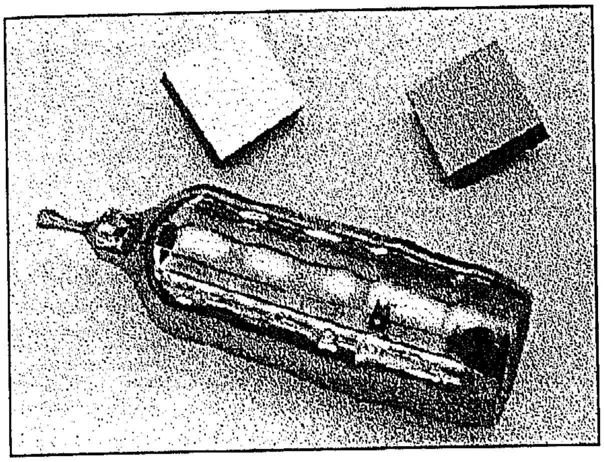

Figure 2. $Si_{1-x}Ge_x$ single crystal of diameter 40 mm and monochromators for the synchrotron radiation based on the graded crystal. The size of monochromators is 30×30 mm.

of the initial charge, it is necessary to grow the crystal with a larger diameter to form a larger concentration gradient. In this case, the crystal will be shorter. Figure 1 shows the distribution of Ge in the length of two crystals of different diameters grown from the melt with identical initial parameters (charge 360 g, 7 at.% Ge). For practical reasons, in order to increase the Ge gradient in the crystal, it is more convenient to decrease the initial charge rather than increase the crystal diameter which can also be restricted by crucible sizes.

Such an approach was successfully used to fabricate monochromators 30 × 30 × 10 mm in size with the highest Ge gradient of 1.4 at.%·cm^{-1} [12] in growing $Si_{1-x}Ge_x$ crystals from the melt with an initial Ge content of 7 at.% (Fig. 2). The grown crystals were 38 to 40 mm in diameter. To fabricate the monochromator, we used a part of the crystal between $g_{\min} \approx 0.65$ and $g_{\max} \approx 0.85$. However, to obtain a constant gradient over the larger length of the crystal, it is already insufficient to vary its size (length and/or diameter) only.

4. Growth of crystals with variable cross section

Let us assume that our goal is to grow a crystal with a constant gradient B of doping impurity or the second component over its length. For $Si_{1-x}Ge_x$, this means that

$$\frac{\partial C_{\mathrm{Ge}}}{\partial L} = B, \quad (3a) \quad \text{or} \quad C_{\mathrm{Ge}} = BL + kC_{0,\mathrm{Ge}}. \quad (3b)$$

Let us find now the shape of the crystal as the dependence $R(L)$. Equating the right-hand sides of expressions (1) and (3b), we can find the relationship between g and L,

$$g = 1 - \left(\frac{B}{kC_{0,\mathrm{Ge}}} L + 1\right)^{1/(1-k)}. \tag{4}$$

At the same time, we can obtain from expression (2) that

$$\frac{\partial g}{\partial L} = \frac{\pi \rho_{\mathrm{cr}}}{M_0} R^2(L), \tag{5}$$

where $R(L)$ is the length dependence of the radius for the crystal of an arbitrary shape. Now, from expressions (4) and (5), we can find the final equation

$$R(L) = \sqrt{\frac{M_0 B}{\pi \rho_{\mathrm{cr}}(1-k)\, C_{0,\mathrm{Ce}}} \left(\frac{B}{kC_{0,\mathrm{Ge}}} L + 1\right)^{\frac{2-k}{k-1}}}. \tag{6}$$

It is noteworthy that Eq. (6) is correct for each impurity with $k \neq 1$.

Figure 3 shows the graded $Si_{1-x}Ge_x$ crystal grown in order to attain the linear Ge distribution in the crystal length. The required gradient of Ge $B \approx 0.8$ at.%·cm^{-1} should be retained over a length of 8 cm. The distribution profile was calculated from Eq. (6) for the following parameters: $B = 0.8$ at.%·cm^{-1}, the initial charge $M_0 = 215$ g, the initial Ge concentration in the melt $C_{0,\mathrm{Ge}} = 7$ at.%, $k = 0.32$, and $\rho_{\mathrm{cr}} = 2.33$ g·cm^{-1}. Here, we did not take into account that the crystal density changes as the Ge concentration in the crystal increases. The calculated curve is given for the range $0.2 < g < 0.9$; the crystal was grown to $g = 0.89$.

One can see from the comparison of the calculated profile and the shape of the grown crystal that they coincide well in the middle part of the crystal. This fact is also confirmed by Fig. 4 which presents the experimental Ge distribution in the crystal length. In the middle

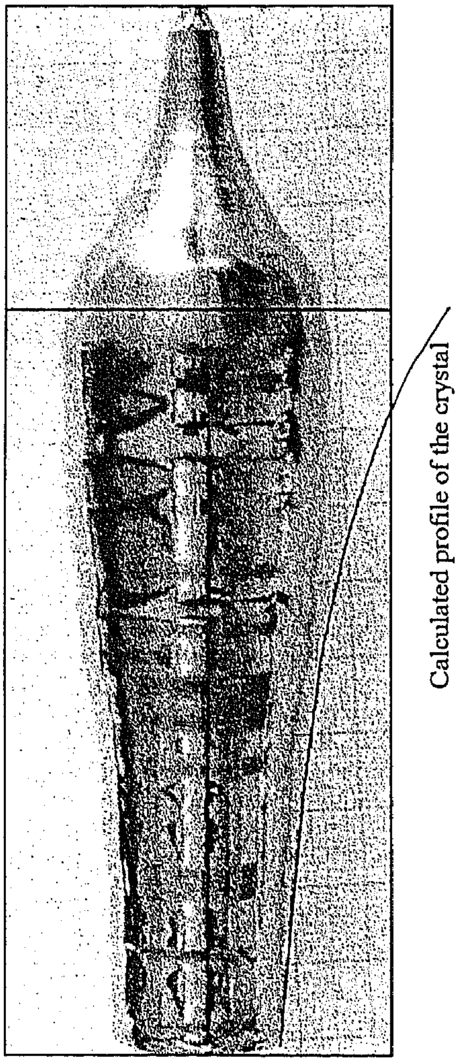

Figure 3. Graded crystal $Si_{1-x}Ge_x$ and the calculated profile for attaining the gradient ~ 0.8 at.%·cm^{-1} (see explanation in text). The horizontal straight line corresponds to the beginning of the experimental curve of the Ge distribution in the length of the crystal in Fig. 4.

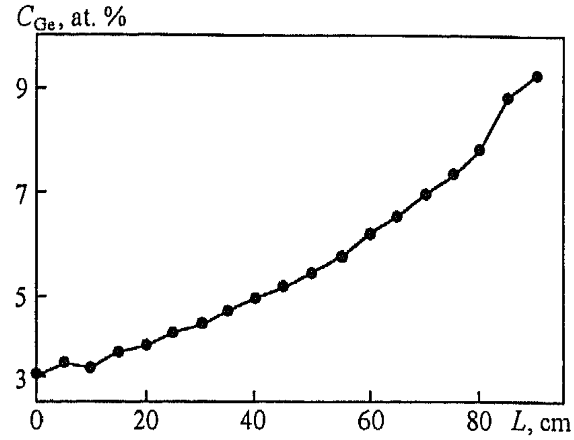

Figure 4. Distribution of Ge in the length of the $Si_{1-x}Ge_x$ crystal shown in Fig. 3. The crystal was grown from the melt with an initial Ge concentration of 7 at.%.

part of the crystal, the Ge distribution in the length is practically linear. The deviation from the linear distribution in the end of the crystal is caused by the fact that the crystal diameter exceeds the calculated one which is 24.4 mm. This was done specially since the crystal diameter should provide the fabrication of the monochromator 20 mm wide. The deviation at the initial stage is also almost inevitable under the condition of obtaining the specified gradient in a length of 80 mm.

The growth of the crystals with the specified shape of the surface is possible only under the automated control of the diameter during growth. As was mentioned above, the maintenance of the specified crystal shape was performed using the automated system with the weight sensor. The main principles of operation of this system were formulated previously [13]. To grow the crystals with a decreasing diameter, we used a program for the final stage of crystal growth by the Czochralski method (the program of the inverse cone), which provides smoothness of the crystal profile via a gradual decrease in the absolute value of the convergence angle from the highest to the lowest value [14]. This exactly corresponds to the growth conditions of the $Si_{1-x}Ge_x$ crystals with a constant Ge gradient (see the calculated profile of the crystal in Fig. 3). The program of a decrease in the crystal radius was switched on when the crystal became cylindrical at $g \approx 0.3$.

The growth of the narrowing crystal by the Czochralski method is associated with difficulties caused by instability of a meniscus since its height is larger than that during widening of the crystal and during growth of the cylindrical part [15]. In this case, the meniscus is subjected to both capillary (mechanical) and thermal instability. The meniscus can break during growth due to the mechanical instability. The thermal instability complicates the control of the growth using the weight sensor. Therefore, the controlling parameters were chosen so as to avoid large jumps of power providing its decrease during growth.

5. Conclusions

The method of growth of the $Si_{1-x}Ge_x$ graded crystals presented in this work allowed us to extend the field of application of the Si:Ge solid solutions. The existence of the lattice parameter gradient which is caused by the variation in the Ge concentration over the crystal length increases the efficiency of monochromators of synchrotron radiation due to the compensation of convergence of the X-ray beam. Since the distance between the radiation source and monochromator can be different depending on the design of the radiation line, the gradient should be optimized for each concrete case. Specifically, for a distance of 20 m, the gradient ~ 1.2 at.%$\cdot$cm^{-1} is optimal [6].

We showed that the gradient can be controlled via the selection of the size and shape of the growing crystal. For example, the growth of a crystal with a diameter decreasing according to a specified law provides a constant gradient over a substantial length. However, it should be noted that the larger the required gradient, the shorter is the length over which it is obtained. Thus, the gradient ~ 0.8 at.%$\cdot$cm^{-1} was obtained over a length of 8 cm. The highest gradient 1.4 at.% Ge$\cdot$cm^{-1} with retention of crystal quality was obtained over a length of 30 mm.

When using silicon monochromators, the (111) and (220) reflections are most often used. This means that the growth direction of the $Si_{1-x}Ge_x$ crystals should be chosen so that crystallographic planes {111} or {110} are parallel to the crystal axis. For (220) monochromators, the crystals were grown in the $\langle 111\rangle$ and $\langle 100\rangle$ directions. For the (111) monochromators, possible directions of the crystal growth are $\langle 110\rangle$ and $\langle 112\rangle$. However, in the growth in the $\langle 110\rangle$ direction, researchers failed to obtain the necessary crystal quality because of dislocation intergrowth from the seed [16]. In the growth in the $\langle 112\rangle$ direction, we succeeded to obtain the crystal quality satisfying the requirements for the fabrication of monochromators.

The (220) and (111) monochromators fabricated from the $Si_{1-x}Ge_x$ graded crystals were used to equip a KMS-2 radiation line at the Berlin Synchrotron Radiation Source. Due to the use of the $Si_{1-x}Ge_x$ graded crystals, the spectral reflectance of monochromators was increased by a factor of 6 as compared with the monochromators from pure Si with retention of the magnitude of the integral reflection. The spectral resolution of the monochromator $\Delta\lambda/\lambda = 2\cdot 10^{-4}$ for the (111) reflection and $\Delta\lambda/\lambda = 10^{-4}$ for the (220) reflection in the spectral range from 3.5 to 15 keV [7].

References

1. Gaworzewski P., Tittelbach-Helmrich K., Penner U., and Abrosimov N.V. *J. Appl. Phys.* 1998, **83**, 5258.
2. Budtz-Jørgensen C.V., Kringhøj P., Larsen A.N., and Abrosimov N.V. *Phys. Rev. B* 1998, **58**, 1110.
3. Pomozov Yu.V., Sosnin M.G., Khirunenko L.I., et al. *Semicond.* 2000, **34**, 989.
4. Mesli A., Vileno B., Eckert C., et al. *Phys. Rev. B* 2002, **66**, 045206.
5. Markevich V.P., Peaker A.R., Murin L.I., and Abrosimov N.V. *J. Phys.: Condens. Matter* 2003, **15**, 2835.
6. Erko A., Schäfers F., Gudat W., Abrosimov N.V., et al. *Nucl. Instrum. Methods A* 1996, **374**, 408.
7. Erko A., Abrosimov N.V., and Alex V. *Cryst. Res. Technol.* 2002, **37** (7), 685.
8. Abrosomov N.V., Rossolenko S.N., Alex V., et al. *J. Cryst. Growth* 1996, **166**, 657.
9. Dismukes J.P. and Yim W.M. *J. Cryst. Growth* 1974, **22**, 287.
10. Abrosimov N.V., Rossolenko S.N., Thieme W., et al. *J. Cryst. Growth* 1997, **174**, 182.
11. Donecker J., Gerhardt A., and Wollweber J. *Mater. Sci. Eng. B* 1994, **28**, 18.
12. Erko A., Packe I., Gudat W., et al. *Nucl. Instrum. Methods A* 2001, **467–468**, 623.
13. Rossolenko S.N. *BRAS Phys.* 1994, **58** (9), 1491.
14. Satunkin G.A., Rossolenko S.N., Kurlov V.N., et al. *Cryst. Res. Technol.* 1986, **21**, 1257.
15. Tatarchenko V.A. Stable Growth of Crystals. Moscow: Nauka, 1988 [in Russian].
16. Alex V., Abrosimov N.V., and Rossolenko S.N. *Inst. Phys. Conf. Ser.* 1997, **160**, 313.