Growth of $Si_{1-x}Ge_x$ Bulk Crystals

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Solid solutions from the SiGe system have become a material candidate for a wide range of applications in the future, for example microelectronics and solar energy conversion. Besides the features well suited for applications and devices, there is also an interest for basic research due to the band structure of SiGe.

. Owing to the physical properties it is very difficult to grow large single crystals from the melt. Using a conventional FZ-technique SiGe single crystals up to 15 at% Germanium and 15 mm in diameter were grown. $Si_{1-x}Ge_x$ single crystals ($0 < \chi < 0.15$) with diameter up to 2 in were grown by conventional Czochralski technique. Although the phasediagramm SiGe is well known since a long time growth of greater volume crystals was impossible and a great challenge for a crystal grower.

A review about the state of the growth art of SiGe crystals is given in the table:

Method	**Si-conc.**	**Remarks**	**References**
Floating Zone	> 75 at%	>92 at% distraction free 20 mm ∅	96WOL, 97SCH
Micro-pulling-down	> 94 at%	concentration gradient (controlled)	096KOH
Bridgman	40 at%	monocrystallin starting region	94DAH
Czochralski	<64 at%	only monocrystallin regions	95YON
Bridgman	< 40 at%	partiell monocrystallin without seed	97KAD
Czochralski	> 85 at%	monocrystallin 50 mm ∅	97ABR
Czochralski	< 92 at%	monocrystallin 38 mm ∅	96ABR

From phase diagram of the SiGe system can be seen a large deviation between liquidus and solidus line. For that reason a high temperature gradient at the solid-liquid interface is necessary to avoid constitutional supercooling during growth from the melt. Moreover there are no „wall-effects" caused by a crucible in the RF-heated FZ-technique. Nevertheless the critical growth rates decrease by more than one order of magnitude than for pure Silicon to maintain single-crystallinity.Several methods for the preparation of a feed rod has been attempted, because no pyrolytic deposited material was available. As one possibility a pure Silicon rod placing pure Germanium into holes was used. The main difficulty arose from the difference of the melting points both Silicon and Germanium. Good mixing in the melt is provided by the strong electromagnetic stirring forces.

Most of the $Si_{1-x}Ge_x$ crystals were grown in [111] direction, a few in [100], with a specific resistance in the order of 10 Ωcm p-type. The growth process started with pure Silicon t avoid zone instabilities during the necking, and so solve the seed problem. After a few millimetres grown with Silicon the Germanium was added, so that several crystals show an axial gradient in the Germanium content. The length of the $Si_{1-x}Ge_x$-single crystals ranged from 30 to 200 mm.

$Si_{1-x}Ge_x$-single crystals more than about 10 mm in diameter exhibit a growth facet. Such facets coinciding with (111) faces (for growth direction [111]) show a different growth mechanism with a critical supercooling value greater than for non-faceted areas. Resulting growth rates may cause constitutional supercooling and lead to polycrystalline growth.

The CZ technique allowed the growth of $Si_{1-x}Ge_x$ single crystals 2 in. in diameter with Ge content up to $\chi = 0.15$ and the growth of $Ge_{1-x}Si_x$ crystals with χ up to $\chi = 0.3$. Single crystalline growth of $Ge_{1-x}Si_x$ crystals was observed up to the Si content $\chi = 0.1$.

For the growth of the $Ge_{1-x}Si_x$ crystals the technique based on the continuous feeding the Ge melt with Si rods was developed. The choice of the movement rate of the Si rods allows to control the change of Si concentration in $Ge_{1-x}Si_x$ crystals with a greater Si content. In the case of a crystal growth the movement rate of rods was about 1.8 times higher then during the growth of a crystal with a lower Si content. One of the problems in the growth of $Ge_{1-x}Si_x$ crystals is the absence of the model of Si transport to the solid-liquid interface during dissolution of Si rods. A delay up to some hours was observed between the first contact of Si rods with Ge melt and appearance of Si in the crystal. Therefore, to improve the growth process it is necessary to investigate the mass transport in the system Si rods-melt-crystal in dependence on the process parameters such as rotation rates of the crystal and the crucible, geometry of the crucible, volume of the melt, form and shape of the feeding rods.

For the determination of the Germanium content different methods were used. Measurements using an IR-Fourier-spectrometer agree well with the following techniques. EDX-measurements provide both, the Germanium distribution and three kinds of striations. One type is associated to the rotation and growth velocity of the crystals during the process. Furthermore precision density measurements were performed for comparison.

Etching was used to investigate the distribution and the amount of defects. Often the density of etch pits varied from 10^1 to 10^5 per cm^2. A dependence of the EPD to the Germanium distribution could not be proved.

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