

## Bulk Single Crystal Growth of Silicon-Germanium

RICHARD H. DEITCH, STEPHEN H. JONES, and THOMAS G. DIGGES, Jr.

Virginia Semiconductor, Inc., 1501 Powhatan Street, Fredericksburg, VA 22401 USA;  
website: www.virginiasemi.com

Si-Ge single crystals up to 68 mm diameter and up to 17 at.% germanium were grown using a modified Czochralski technique. Pre-grown large diameter single crystal silicon seeds with various crystallographic orientations were used as templates for solidification to reduce cap crystallization time and to ensure single crystallinity at desired crystal diameters. A discussion is presented of the influences of seed preparation, crystal growing parameters and post-growth processing on the Si-Ge bulk single crystals produced using this new technique. The modified Czochralski technique described in this paper is ultimately intended for the manufacture of 100–200 mm diameter Si-Ge substrates.

**Key words:** Czochralski growth, Si-Ge, solid solution alloy, semiconductors, substrate

### INTRODUCTION

Recently, there has been a substantial increase in the number of publications concerning Si-Ge single crystal growth. Although most have dealt with the preparation of thin films on silicon substrates, there has also been progress reported on the growth of various compositions of this alloy in bulk form using the Czochralski (CZ)<sup>1–6</sup> and other related methods.<sup>10–14</sup> Si-Ge alloys are of interest because they have higher mobility than silicon and can be produced with bandgaps between those of silicon and germanium. Uses for single crystals include substrates for epitaxy, photodetectors, solar cells, high-performance discrete devices, and other electronic and photonic devices. The immediate goal of this work was to obtain at least a 50 mm diameter Si-Ge single crystal with relatively high germanium content using a standard CZ technique, and, if possible, without making furnace design modifications. The long range goal of this research is to create the technology needed for manufacturing 100–200 mm diameter Si-Ge substrates.

The equilibrium phase diagram of Fig. 1 for the Si-Ge binary system is of the isomorphous type. It shows that complete solubility exists between the two elements in both the liquid and solid states. From a liquid consisting of 40 at.% germanium, the first solid to form upon cooling to 1300°C will contain about

17 at.% germanium. With continued cooling under equilibrium conditions, the germanium concentration in the liquid will increase as defined by the liquidus, and the germanium concentration in the solidifying alloy will move along the solidus also towards higher germanium values. However, in the case of CZ growth, the first solid to form will have a slightly lower germanium content than indicated by the solidus.<sup>2,5</sup> In addition, as temperature is reduced, the amount of germanium in the solid will not increase as fast as indicated by the slope of the solidus. Uniformity of composition with crystal length can be improved by adding silicon to the liquid as growth occurs.<sup>4</sup> It also can be improved by increasing the volume of liquid from which a particular volume of solid is grown. Alternatively, the germanium composition gradient can be increased either by adding germanium to the liquid during growth<sup>10</sup> or by reducing the starting volume of liquid.

Since the Si-Ge system exhibits a large liquidus-solidus gap, low pulling rates, usually well below 2 mm per hour, are needed to prevent the onset of dendritic growth. Standard pulling rates to grow elemental silicon from its melt are on the order of 2–10 cm per hour. Thus, when using a conventional CZ method for growing a Si-Ge single crystal, it can take forty times longer than it does for silicon to grow a cap to the same diameter. Initial attempts were made to grow a Si-Ge single crystal using the standard CZ technique of necking followed by cap growth

(Received October 15, 1999; accepted April 5, 2000)



and then body growth. Although it was possible to crystallize slowly enough to avoid dendritic growth, the nucleation of randomly-oriented crystals at the circumference of a growing cap made it difficult to increase the size of an alloy single crystal much beyond the 6 mm diameter of the seed. To prevent such nucleation, it appeared that it might be necessary to use special cap growth techniques, such as slowly growing a cap with a cone shape;<sup>4</sup> to make furnace design modifications, such as to deflect the flow of helium away from both the liquid and the crystal;<sup>5</sup> or to use an encapsulant.<sup>11,12</sup> However, it was observed that the crystals that were nucleated during cap growth did not extend very far into the seeded Si-Ge single crystal, and that they did not propagate much towards the center as a boule grew longer. Therefore, the following approach was taken in an effort to produce a large diameter Si-Ge single crystal.

It was conjectured that, if growth of an alloy single crystal could be seeded at a sufficiently large diameter, and, if that diameter could be maintained by proper adjustment of growth parameters, a single crystal of significant length would result regardless of the existence of a ring of small crystals at the periphery. The time normally required to crystallize a cap could, instead, be applied to growing a longer boule, and the small crystals could be ground away to obtain Si-Ge having only the seeded orientation. Presented here are results of experiments that were conducted to evaluate this approach. The large diameter zero-dislocation silicon seeds required for this evaluation were obtained from previously-grown CZ crystals.

#### EXPERIMENTAL PROCEDURE

A CZ furnace with RF heating was used to grow the Si-Ge single crystals. A silica crucible 18 cm in diameter was filled with either silicon and germanium pieces or previously solidified Si-Ge alloy to provide a total charge of 1500 gm. Helium was introduced into the furnace chamber and maintained at a pressure of one atmosphere. After heating for about one hour to form a Si-Ge liquid solution and removing surface contamination, the temperature was stabilized above the liquidus for the corresponding charge composition. An excess seed diameter of about 15 mm was needed to allow for a slight diameter reduction at the start of growth as well as for the ring of crystallites expected to form at the periphery.

The silicon seed was rotated clockwise at a constant rate between 5 rpm and 30 rpm; the crucible was rotated at a constant rate either clockwise or counter-clockwise between 4 rpm and 20 rpm. Referring to Fig. 1, the temperature of the alloy liquid was first stabilized above that of the liquidus for its composition. Next, the seed was lowered to a position just above the surface of the liquid for preheating. Then, the seed was immersed to a position where its maximum diameter was at the same level as the liquid surface. As a result, some dissolution of the silicon seed occurred. When the amount of silicon in the liquid increased enough to reach the liquidus, small

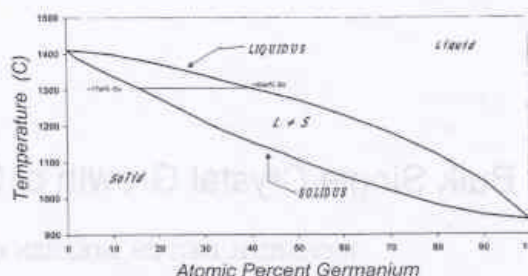


Fig. 1. The complete solubility that exists between silicon and germanium is shown by the equilibrium phase diagram.

thermal fluctuations at the solid-liquid interface produced crystallization of Si-Ge.

After a meniscus formed, the temperature was adjusted and pulling began at no more than 2 mm per hour. The crucible was not lifted and, as pulling continued, the growing alloy body diameter became slightly smaller than the maximum seed diameter. Thereafter, the body diameter could be controlled by slowly lowering the temperature. After growth, a boule was raised slightly above the liquid surface and furnace cooled. There were times when multiple boules were grown in a single batch crystal growing process by utilizing more than one seed. In those cases, shorter boules were produced and only the last grown was furnace cooled. The others were raised slowly from the hot zone and kept for one hour inside the bellows before being cooled to room temperature outside the furnace.

Most crystals were grown with a (100) orientation, but seeded (111), (110), and (211) crystals also were produced. The Si-Ge boules were epoxy mounted to graphite rails and wafers having surfaces perpendicular to the pulling direction were cut using an ID diamond saw. Then, after having been edge rounded, the wafers were etched in KOH to remove damage and delineate polycrystallinity. Crystallographic orientation was determined by x-ray diffraction using the back-reflection Laue method. Electrical resistivity was measured by the four-point probe method of ASTM F84-84a, and conductivity type was determined by the hot-probe method of ASTM F42-87. Some wafers were polished either on one or on both sides for further evaluation. The surface smoothness was evaluated by atomic force microscopy (AFM), and chemical composition was determined either by calculating density, by energy dispersive x-ray (EDX) spectroscopy, or by Vis-UV absorption. Polished wafers were immersed for ten minutes in a modified Schimmel etch as described in ASTM F47-87 to reveal crystallites, cellular structure, and striations, as well as to determine defect density and distribution by optical microscopy.

#### RESULTS AND DISCUSSION

Silicon seeds with increasingly larger diameters were used to initiate growth until a 68 mm diameter alloy single crystal was obtained. As is the case for



unintentionally-doped CZ silicon, these Si-Ge crystals contained varying amounts of carbon, oxygen, boron, and phosphorus. They were found to be either n-type (7–59 ohm cm) or p-type (10–67 ohm cm).

Figure 2 shows a Si-Ge boule that was grown from a silicon seed having a maximum diameter of 28 mm. It is tapered because the temperature was not reduced as it was being pulled. Figure 3 shows a relatively constant diameter Si-Ge boule that was grown starting with a 65 mm diameter silicon seed. It can be seen that alloy deposited around the seed before crystal pulling began. If the temperature of the liquid had been higher when the seed was immersed, as it had been for the boule shown in Fig. 2, alloy deposition around the seed would not have occurred.

Depending on the shape of the seed and how it had dissolved in the liquid, various transitions from sili-

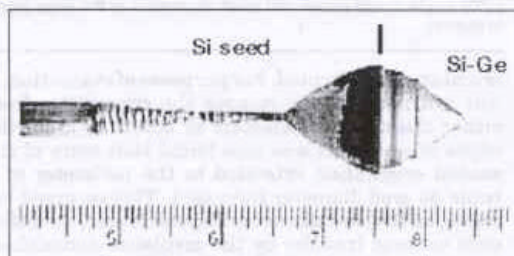


Fig. 2. This tapered Si-Ge single crystal was pulled using a large diameter silicon seed. The temperature was not lowered after immersion (scale in inches).



Fig. 3. This Si-Ge single crystal was pulled using a large diameter silicon seed. The temperature was lowered after immersion to maintain diameter (scale in inches).

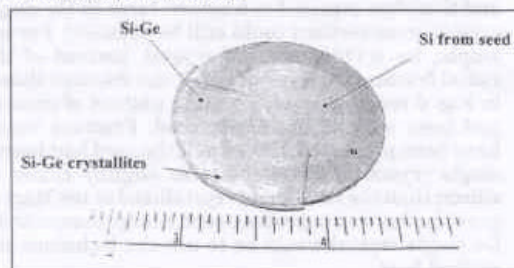


Fig. 4. This 40 mm diameter water (epoxy mounting not completely removed) shows a portion of the original silicon seed surrounded by a Si-Ge single crystal with the seeded crystallographic orientation. Also shown for this non-furnace cooled material are porosity, edge polycrystallinity and radial fracture (scale in inches).

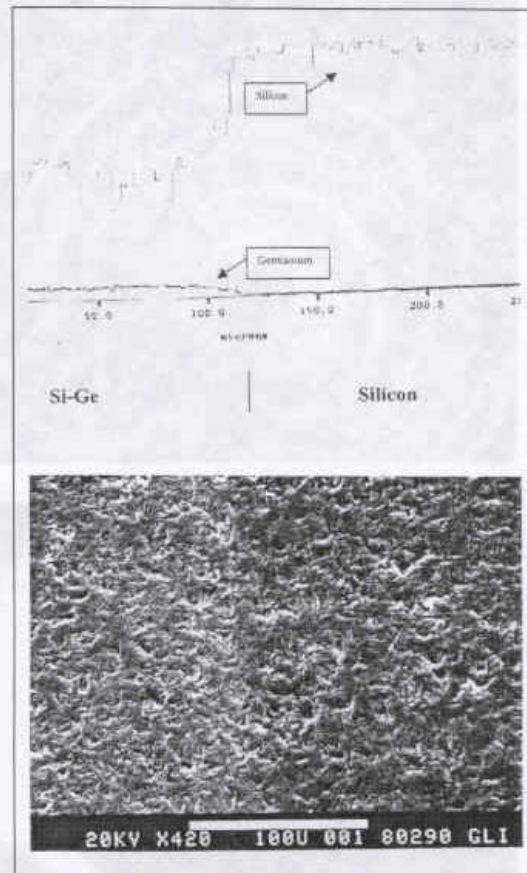


Fig. 5. This photograph and compositional (EDX) data show the change in composition across an alloy/silicon radial boundary in an as-cut water.

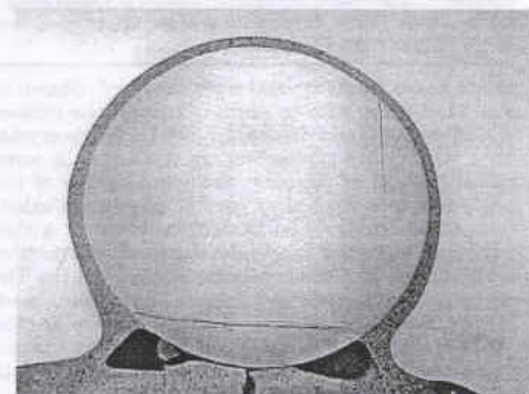


Fig. 6. Fracture along non-radial directions can be seen in this 44 mm diameter Si-Ge water (epoxy mounting not removed) that was cut from a non-furnace cooled boule. A specially shaped silicon seed was used to initiate growth (compare to Fig. 4).



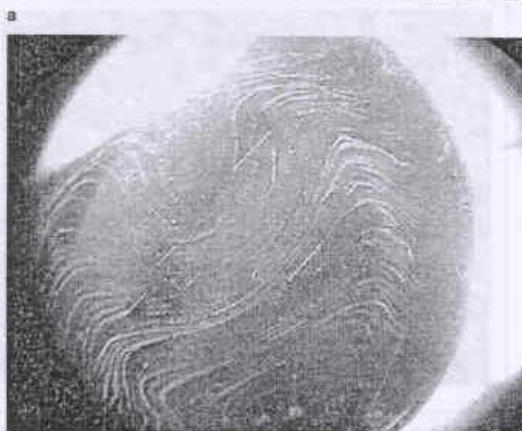
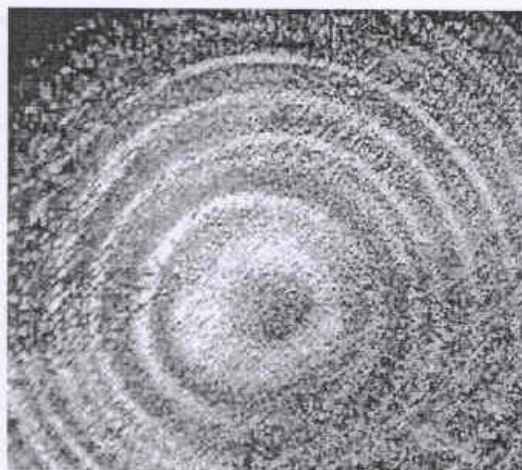


Fig. 7. These etched Si-Ge single crystal wafers show the influence that seed/crucible rotations can have on striations and defect distribution: (a) counter-rotation, 10 mm diameter wafer, 10X; (b) iso-rotation, 30 mm diameter wafer, 3X.

con to Si-Ge single crystal were observed. Shown in Fig. 4 is a wafer with an undissolved circular portion of a silicon seed surrounded by a Si-Ge single crystal zone with Si-Ge crystallites at the edge. In some cases, instead of circular, the cross-section of the original silicon seed after partial dissolution exhibited a non-circular shape. In all cases, however, within a few millimeters of longitudinal growth, the circular cross-section of a boule became entirely Si-Ge. The porosity observed in Fig. 4 occurred only near a seed/alloy interface and could be avoided by controlling the shape of the seed. The change in composition across a radial seed/alloy boundary is shown by the EDX data of Fig. 5.

Even though all of the Si-Ge boules that were grown exhibited some peripheral cellular structure or crystallites, interference with the seeded crystallographic

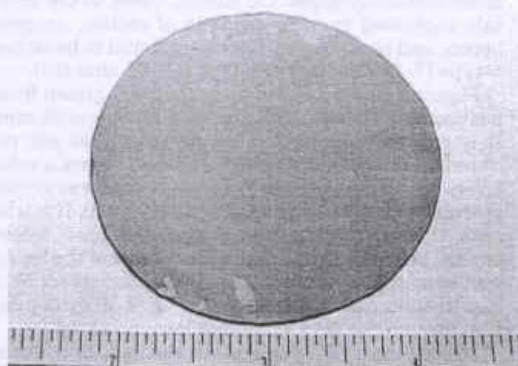


Fig. 8. This as-cut Si-Ge wafer has an approximately 50 mm diameter (100) single crystal center and small crystallites at the edge (scale in inches).

orientation was limited. For purposes of evaluation, it was not necessary to remove the crystallites from either the outside diameters of boules or from the edges of wafers. It was also found that more of the seeded orientation extended to the perimeter of a boule as seed diameter increased. This occurred because, as the seed diameter became larger, the influence on heat transfer by the meniscus diminished, and the top of the seed became more effective in deflecting the flow of helium. It appears possible, therefore, that, at some larger diameter than 68 mm, a Si-Ge single crystal without cellular structure or crystallites at its periphery can be grown using the seeding technique described here.

Although the use of large diameter seeds eliminated problems associated with cap growth, a problem that was introduced was fracture on cooling caused by the difference between the coefficients of thermal expansion of silicon and the Si-Ge alloys. For those alloy compositions that were grown, it was found that fracture did not occur until boule diameter exceeded 25 mm. For the larger diameter boules, fracture was prevented by furnace cooling. However, for those boules that were not to be furnace cooled, and therefore expected to fracture, large Si-Ge single crystal cross-sections could still be obtained. For example, for a (100)-oriented crystal, instead of the radial fracture observed in Fig. 4, the fracture shown in Fig. 6 resulted when a certain pattern of grooves had been cut into the silicon seed. Fracture would have been prevented, however, if the seed had been a single crystal of Si-Ge that was slightly richer in silicon than the alloy being crystallized at the start of growth. One way to produce such a large diameter Si-Ge single crystal would be to use the technique described here.

When using a large diameter seed, the liquid is stirred at a constant and relatively high rate from the beginning of solidification, and the large cooled cap provides a steep temperature gradient. Both of these

conditions are desirable for good crystal growth because they stabilize the growth interface and prevent constitutional supercooling. A defect density on the order of  $10^4$  per  $\text{cm}^2$  was measured and, as shown in Fig. 7, defect distributions usually followed striation patterns. Concentric striations were observed when the seed and crucible were counter-rotated (Fig. 7a). Non-concentric striations, like those shown in Fig. 7b, could be obtained when the seed and crucible were iso-rotated at certain relative rates. Defects having the appearance of stacking faults and isolated areas of cellular structure were found near the circumference on some wafers. This was an indication that strain produced in boules by radial thermal gradients during cooling had not been fully relaxed. Post-growth annealing of such boules probably would be useful in preventing fracture that otherwise would occur upon grinding and cutting. Figure 8 shows a 63 mm diameter wafer cut from a boule that was grown using the seeding technique described here. Peripheral crystallites can be seen surrounding an entirely (100) central area that is approximately 50 mm in diameter. Vis-UV measurement indicated the same bandgap at different positions across this wafer and large area AFM scans revealed no features greater than 2 nm high on a polished surface.

### CONCLUSIONS

A Czochralski crystal growing technique was used to consistently produce up to 68 mm diameter Si-Ge bulk single crystals with various crystallographic orientations and with concentrations up to 17 at.% germanium. Pre-grown large diameter silicon seed crystals were used as single crystal templates for alloy solidification to reduce cap crystallization time and provide single crystallinity at desired crystal diameters. Defect densities on the order of  $10^4$  per  $\text{cm}^2$  have been achieved. This technique will be used to obtain lower defect density and larger diameter sub-

strates, and it is anticipated that Si-Ge single crystals with compositions covering the entire range from pure germanium to pure silicon will be grown. Virginia Semiconductor, Inc. has a U.S. patent pending on the technology described in this paper.

### ACKNOWLEDGEMENTS

The authors thank B. Hizer, R. Bromme, M. Shelton, L. Holder, K. Gould, and K. Heath for assistance, and are grateful to John Berger of the University of Delaware, J.C. Bean of the University of Virginia, W.C. Hughes of James Madison University, and E. Borguet of the University of Pittsburgh for material characterizations.

### REFERENCES

1. M. Kurten and J. Schilz, *J. Cryst. Growth* 139, 1 (1994).
2. I. Yonenaga, A. Matsui, S. Tozawa, K. Sumino, and T. Fukuda, *J. Cryst. Growth* 154, 275 (1995).
3. N.V. Abrosimov, S.N. Rossolenko, V. Alex, A. Gerhardt, and W. Schroder, *J. Cryst. Growth* 166, 657 (1996).
4. N.V. Abrosimov, S.N. Rossolenko, W. Thieme, A. Gerhardt, and W. Schroder, *J. Cryst. Growth* 174, 182 (1997).
5. A. Matsui, I. Yonenaga, and K. Sumino, *J. Cryst. Growth* 183, 109 (1998).
6. I. Yonenaga and M. Nonaka, *J. Cryst. Growth* 191, 393 (1998).
7. I. Yonenaga and Y. Murakami, *J. Cryst. Growth* 191, 399 (1998).
8. R.H. Deitch, S.H. Jones, and T.G. Digges, Jr., *MRS 1999 Fall Meeting* (Warrendale, PA: MRS, 1999).
9. R.H. Deitch, S.H. Jones, and T.G. Digges, Jr. (Paper presented at the 1999 Intl. Semicond. Device Research Symp., Charlottesville, VA, 1-3 December 1999).
10. J. Wollweber, D. Schulz, and W. Schroeder, *J. Cryst. Growth* 163, 243 (1996).
11. K. Kadokura and Y. Takano, *J. Cryst. Growth* 171, 56 (1997).
12. D. Bliss, B. Demczyk, A. Anselmo, and J. Bailey, *J. Cryst. Growth* 174, 187 (1997).
13. P. Dold, A. Barz, S. Recha, K. Pressel, M. Franz, and K.W. Benz, *J. Cryst. Growth* 192, 125 (1998).
14. J. Schilz and V.N. Romanenko, *J. Mater. Sci.: Mater. in Electron.* 6, 265 (1995).