METALLIC CRUCIBLE SINGLE CRYSTAL GROWTH OF SILICON BY CZOCHRALSKI METHOD

[1]Vijay Maurya, [2]Anuj Verma
[1]Assistant Professor, [2]Assistant Professor
[1]Electronics Engineering Department, [2]Electrical Engineering Department
[1]Institute of Engineering & Technology, Lucknow, [2]International Maritime Institute, Greater Noida, India

Abstract: Czochralski (CZ) process, which accounts for 80% to 90% of worldwide silicon consumption, consists of dipping a small single-crystal seed into molten silicon and slowly withdrawing the seed while rotating it simultaneously.

The Czochralski method, invented by the Polish scientist J. Czochralski in 1916, is the method of choice for high volume production of Si single crystals of exceptional quality and shall be discussed briefly. To start growing a "Czochralski crystal" by filling a suitable crucible with the material, here hyper pure correctly doped Si pieces obtained by crushing the poly-Si from the Siemens process. Care has been taken up to keep impurities out by doing it in clean room and use hyper pure silica for your crucible.

There are three major stages involved in this research. The first is the production of pure materials and improved equipment associated with the preparation of these materials. The second is the production of single crystals first in the laboratory and then extending it to commercial production. The third is the characterization and utilization of these crystals in devices. We focus on a Czochralski crystal growth process to produce a 0.7 m long radius of 0.5m. The process is comprised of a rotating pedestal that can move in the axial direction. A crucible containing silicon crystals is placed on the pedestal and heaters (placed on the sides of the chamber and under the pedestal) are used to increase the temperature of the Si crystals inside the crucible (through which will smoothly regulate the cooling process of the crystal as it leaves the chamber), after the crystal radius has obtained its final value, and accounts for radiative heat exchange between the crystal, heater shield, crucible, melt surface and the environment.

***Index Terms* – Single crystal growth, Czochralski method, SGS, EGS, Ingot, crucible**

I. INTRODUCTION

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries.

In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly-crystalline material and extra effort is justified because of the outstanding advantages of single crystals (Laudise 1970). The reason for growing single crystals is, many physical properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research. Nonlinear optical crystals are very important for laser frequency conversion (Kurtz 1968). Potassium dihydrogen phosphate (KDP) is suitable for higher harmonic generation of huge laser systems for fusion experiments because it can be grown to larger sizes and also KDP has a high laser damage threshold. Potassium titanyl phosphate (KTP) is a useful nonlinear optical crystal to get efficient green light by the frequency doubling of laser. It has high optical nonlinearity, large temperature and angular allowance and it is non hygroscopic and mechanically hard. The method of growing crystals varies widely; it is mainly dictated by the characteristics of the material and its size (Buckley 1951 and Mullin 1976).The demand for nonlinear optical crystals with superior properties is increasing due to quantum jump in the design of nonlinear optical devices with higher performance.

With the progress in crystal growth technology, materials having attractive nonlinear properties are being discovered at a rapid pace [1]. To enable a material to be potentially useful for non linear optical applications, the material should be available in bulk single crystal form (Bailey 1991). And so, crystal growth of new nonlinear optical materials and investigation into their properties has become most indispensable and efficacious disciplines in the field of materials science and engineering. The rapid development of optical communication system has led to a demand for Nonlinear Optical (NLO) materials of high performance for use as components in optical devices. Non linear optical materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. There are three major stages involved in this research. The first is the production of pure materials and improved equipment associated with the preparation of these materials. The second is the production of single crystals first in the laboratory and then extending it to commercial production. The third is the characterization and utilization of these crystals in devices. In this section, various methods of crystal growth with emphasis on low temperature solution growth technique are described. The solvent to be chosen to grow good quality crystals from solution, the effect of super- saturation and pH value of the solution is also discussed.

II. STATE OF THE ART

With the progress in crystal growth technology, materials having attractive nonlinear properties are being discovered at a rapid pace (Baumert et al 1987, Chemla and Zyss 1987, Gunter et al 1987 and Warren 1990)[1]. To enable a material to be potentially useful for non linear optical applications, the material should be available in bulk single crystal form (Bailey 1991). And so, crystal growth of new nonlinear optical materials and investigation in to their properties has become most indispensable and efficacious disciplines in the field of materials science and engineering. The rapid development of optical communication system has led to a demand for Nonlinear Optical (NLO) materials of high performance for use as components in optical devices. NLO materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. The search for new materials has identified novel semi organic systems of considerable potential and high performance.

III. CZOCHRALSKI CRYSTAL GROWTH PROCESS:

To start growing a "Czochralski crystal" by filling a suitable crucible with the material, here hyper pure correctly doped Si pieces obtained by crushing the poly-Si from the Siemens process. Take care to keep impurities out, do it in a clean room and use hyperpure silica for your crucible. Make sure that the inside of the machine is very clean too and that the gas flow the gas you introduce but also the SiO coming from the molten Si because parts of the crucible dissolve - does not interfere with the growing crystal. Dissolve the Si in the crucible and keep its temperature close to the melting point. Since you cannot avoid temperature gradients in the crucible, there will be some convection in the liquid Si. You may want to suppress this by big magnetic fields. Insert your seed crystal, adjust the temperature to "just right", and start withdrawing the seed crystal. For homogeneity, rotate the seed crystal and the crucible. Rotation directions and speeds and their development during growth, are closely guarded secrets.

First pull rather fast, the diameter of the growing crystal will decrease to a few mm. This is the "Dash process" ensuring that the crystal will be dislocation free even though the seed crystal may contain dislocations. Now decrease the growth rate, the crystal diameter will increase until you have the desired diameter and commence to grow the commercial part of your crystal at a few mm/second.

As crystal grows, the impurity concentration (including the dopants if you do not watch out) will increase in the melt (due to segregation) and therefore also the percentage incorporated into the crystal. The temperature profile of the whole system will also change - you are now deeper down in the crucible and the crystal cools off a little more slowly. All these factor influence the homogeneity of the crystal. The radial and lateral doping level is influenced it will not stay constant without some special measures.

The concentration of impurities, especially interstitial oxygen, may change. Crystal lattice defects still present (essentially agglomerates of the point defects present in thermal equilibrium at high temperatures) may change in size and distribution. So change the rotation speeds, the temperature, and the growth speed. Change all important parameters continuously so that the crystal is homogeneous.

Now the crystal is nearly finished, do not want to use up all the Si, because the "last drop" contains all the impurities not yet incorporated because of their small segregation coefficients.

But you cannot simply pull out the crystal after the desired length has been reached. The thermal shock of the rapidly cooling end would introduce large temperature gradients in the crystal which in turn produce stress gradient plastic deformation (easy in Si at high temperatures) will take place and this means dislocation are nucleated and driven into the crystal. The dislocation will even run up into the formerly dislocation free part of the crystal, destroying your precious Silicon. So you withdraw gradually by just increasing the pulling rate a little bit which will lead to a reduced diameter. The crystal then ends in an "end cone" similar to the "seed cone".

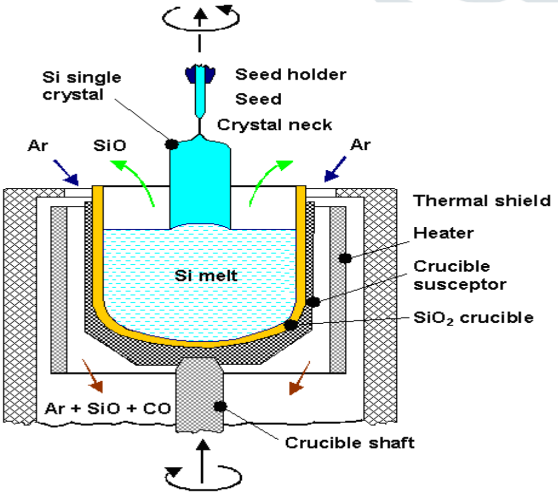

Fig.1 the crucible is usually made of quartz or graphite with a fused silica lining

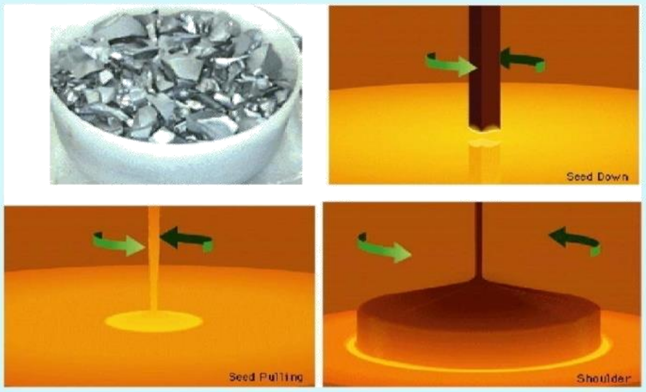

Fig.2 Sequence of photographs and drawings illustrating CZ crystal growth

STAGE 1: PRODUCTION OF PURE MATERIAL: IMPURITY SEGREGATION:

Impurities, both intentional and unintentional, are mixed into the melt during crystal growth, while unintentional impurities originate from the crucible, ambient, etc. All common impurities have different solubility in the solid and in the melt. An equilibrium segregation coefficient k_o can be defined to be the ratio of introduced into the silicon ingot. Intentional dopants are the equilibrium concentration of the impurity in the solid to that in the liquid at the interface i.e. $k_0 = \frac{C_s}{C_l}$

Impurity	Al	As	B	C	Cu	Fe	O	P	Sb
k_o	0.002	0.3	0.8	0.07	$4x10^6$	$8x10^6$	0.25	0.35	0.023

Note that all the values shown in the table are below unity, implying that the impurities preferentially segregate to the melt and the melt becomes progressively enriched with these impurities as the crystal is being pulled.

STEP 2: PRODUCTION OF SINGLE CRYSTALS:

The process of production of single crystal growth can be summarized as shown in fig.3. further each step can be sequentially illustrated by the following figures from fig.4 to fig.7.

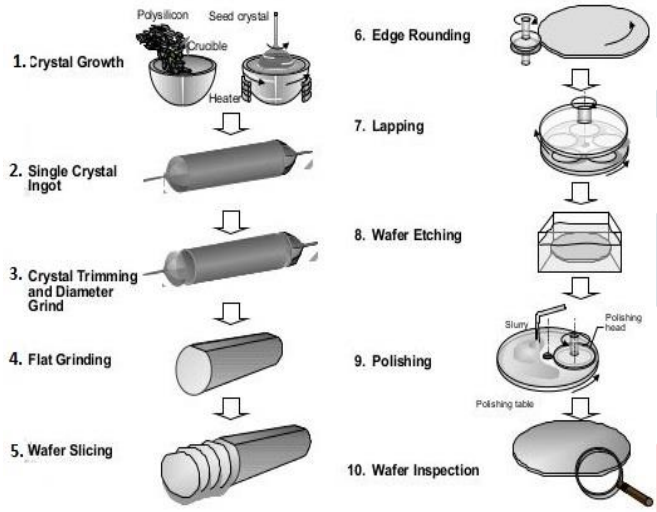

Fig.3 WAFER PREPRATION

Fig.4 SINGLE CRYSTAL INGOT

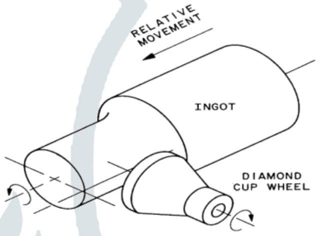

Fig.5 Grinding

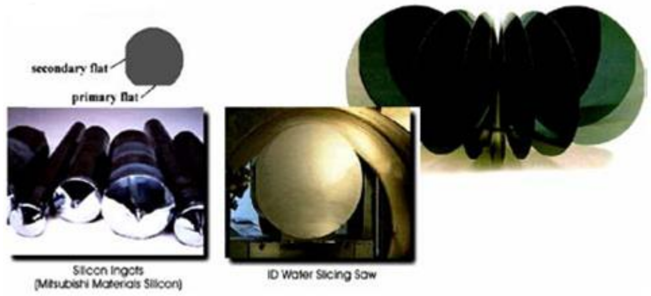

Fig.6 WAFER SLICING

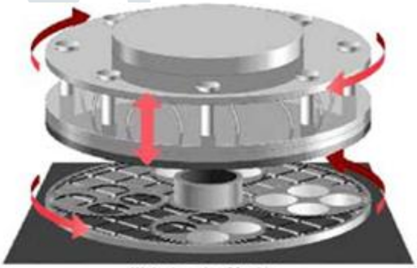

Fig.7 WAFER LAPPING

WAFER ETCHING:

After lapping, wafers are etched in a solution of nitric acid/acetic acid or sodium hydroxide to remove microscopic wax or surface damage created by the lapping process. The acid or caustic solution is removed by a series of high purity RO/DI water baths.

WAFER POLISHING:

The wafers are polished in a series of a combination chemical and mechanical polishing process called CMP. The wafers are held in a hard ceramic chuck using either wax bonding or vacuum and buffed with slurry of silica powder, RO/DI water and sodium hydroxide. The polishing process usually involves two or three polishing steps with progressively finer slurry and intermediate cleaning using RO/DI water is shown in fig.8.

WAFER CLEANING:

Most wafer manufacturer use a final cleaning method developed by RCA in 1970. The 3 step process starts with an SC1 solution (ammonia, hydrogen peroxide and RO/DI water) to remove organic impurities and particles from the wafer surface. Next, natural oxide and metal oxides are removed with hydrofluoric acid, and finally, the SC2 solution, (hydrochloric acid and hydrogen peroxide), causes super clean new natural oxides to grow up on the surface.(fig.9)

Polishing and cleaning is the final step. Its purpose is to provide a smooth, secular surface on which device features can be photoengraved.

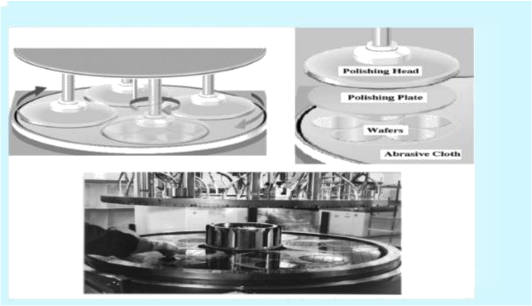

Fig.8 Wafer polishing

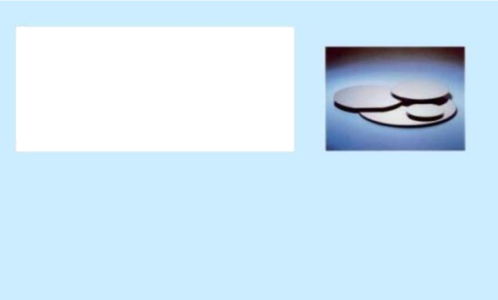

Fig.9 Finished Wafers

IV. CONCLUSION

Here we study about single crystal growth of Silcon by Czochralski method. The main advantage of the Czochralski method is the possibility of fast growth of good quality large single crystals. Moreover, since the crystals are grown using oriented seeds they adopt required orientation. In the typical Czochralski arrangements using high frequency generators the metallic crucible heats the melt and the ceramic thermal shields. The need of crucibles seriously limits applicability of the Czochralski method. Hence the Czochralski method is that by which large single crystals can be grown that is why it is used extensively in the semiconductor industry.

In general this method is not suitable for incongruently melting compounds and of course the need for a seed crystal of the same composition limits its use as tool for exploratory synthetic research.

REFERENCES

[1] Baumert et al (1987), Chemla and Zyss (1987), Gunter et al (1987) and Warren (1990) “Introduction to crystal growth methods”.
[2] T.G. Digges, R.H. Hopkins, R.G. Seidensticker, J. Cryst. Growth 29, 326 (1975)
[3] M. Itsumi, H. Akiya, T. Ueki, J. Appl. Phys. 78, 5984 (1995)
[4] W. von Ammon, E. Dornberger, H. Oelkrug, H. Weidner, J. Cryst. Growth 151, 273 (1995)
[5] L.J. Liu, K. Kakimoto, Cryst. Res. Technol. 40, 347 (2005)
[6] L.J. Liu, K. Kakimoto, Int. J. Heat Mass Transfer 48, 4481 (2005)
[7] V.V. Voronkov, J. Cryst. Growth 59, 625 (1982)
[9] M. Watanabe, M. Eguchi, T. Hibiya, private communication.
[8] V.V. Voronkov, R. Falster, J. Electrochem. Soc. 149, G167 (2002)
[9] L.J. Liu, K. Kakimoto, Int. J. Heat Mass Transfer 48, 4492 (2005)
[10] L. Liu, S. Nakano, K. Kakimoto, J. Cryst. Growth 282, 49 (2005)