REVIEW ARTICLE ON PROPERTIES, GROWTH & APPLICATIONS OF SILICON SEMICONDUCTOR

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ABSTRACT

This paper presents the review of development of silicon as a semiconductor device, its properties, growth techniques used for silicon crystal, applications and latest research done till date. A broad comparison of Czochralski growth method and Floating zone method is presented. Floating Zone method results had a mechanically weaker silicon than that of the Czochralski silicon. Other methods like Czochralski single-crystal growth with applied magnetic field and neckingless growth method are also presented. Various information regarding the work on Silicon semiconductor by prominent scientist iscollected. Si possesses a moderate energy band gap of 1.12eV, which makes it a stable substance. It is used in electronic devices as it can operate in wide high temperature range up to 200^{0}C. Silicon plays a crucial part in information and communication technology, as it is used in manufacturing of components like transistors, diodes, integrated circuits (ICs), microchips, photonics so on. Silicon has carried us into the ultra-large scale integration (ULSI) era and system-on-a-chip (SOC). Paper provides all necessary facts and growing research on the use of Silicon as a semiconductor in rising communication technology

Keywords: Semiconductor; silicon; single-crystal growth; Czochralski method; Floating zone method; Neckingless growth method

1. Introduction

Silicon was first isolated in 1824 by Swedish chemist Berzelius (Berzelius, 1825) [1]. He named the new element Silicium. "Silicon" got its name by Scottish Chemist Thomas Thomson (Thomson, 1817) [2]. He, kept the name 'silicis'. Silicon is the fourteenth element of the periodic table and comes in Group IVA element. Pure silicon is a dark gray solid with the same crystalline structure as diamond. It has a melting point of 14100 C (25700 F), a boiling point of 42710C (23550 F), and a density of 2.33 g/cm3. Naturally, silicon is found linked up with a pair of oxygen molecules as silicon dioxide 'silica'. Silicon is the seventh-most abundant element in the universe and the second-most abundant element on the planet, after oxygen, according to the Royal Society of Chemistry and covers 25 percent of earth's crust. It does not appear as a free element in nature as its chemical affinity is high, so it is produced by chemical reduction process only.

First Semiconductor Effect was recorded by Michael Faraday (Faraday, 1839) [3]. He described the "extraordinary case" of his discovery of electrical conduction increasing with temperature in silver sulphide crystals. Which was opposite to that observed in copper and other metals. Faraday's experimental work in chemistry, also led him to first documented observation of semiconductor. While investigating the effect of temperature on semiconductor on "sulphurette of silver" (silver sulphide) in 1833 he found that electrical conductivity increased with increasing temperature which was opposite of the metals like copper. Semiconductor point contact rectifier was discovered by Ferdinand Braun (Braun, 1874) [4]. When he probed a galena crystal with thin metal wire point, he noted that current flowed freely in one direction only. Thus he discovered the rectification effect. In

1901 semiconductor rectifiers patented as “cat whisker” detectors by Jagdish Chandra Bose (Bose, 1904) [5]. He patented the use of a semiconductor crystal rectifier for detecting radio waves. Field effect semiconductor device concept was patented in 1926 by Julius Lilienfeld (Lilienfeld, 1930) [6].In 1931 “The Theory of Electronic Semi-conductor” (Wilson, 1931)[7] gets published. Alan Wilson (Wilson, 1931) [7] (Wilson, 1932) [8] uses quantum mechanics to explain basic semiconductor properties. After 7 years the three scientist named, Boris Davydov (Davydov, 1938) [9], Nevill Mott (Mott, 1938) [10] and Walter Schottky (Schottky, 1938) [11] independently explains rectification. In 1940 Russell Ohls discovers the p-n junction and photovoltaic effect in silicon that lead to the development of junction transistor and solar cells (Ohl, 1946) [12]. In the year 1941 semiconductor diodes were served in WWII. The techniques for producing high purity germanium and silicon crystals were developed for wartime radar microwave detectors (Scaff & Ohl, 1947) [13]. William Shockley conceived an improved transistor structure based on a theoretical understanding of p-n junction effect (Shockley, 1949) [14]. In 1951 William Pfann and Henry Theurer (Theurer, 1962) [15] developed a zone refining technique for production of ultra-pure semiconductor materials.

A transistorized computer prototype demonstrates the small size and low-power advantages of semiconductors. James R. Harris (Harris, 1958) [16] designed and built a transistorized computer dubbed Transistor Digital Computer (TRADIC) for the U.S. Air Force in 1954.Silicon devices that function from -55 to 125^{o}C became possible after the supply of high-purity semiconductor-grade material. In 1954 Morris Tanenbaum (Tanenbaum, 1954) [17] fabricates the first Si transistor at Bell Labs but Texas Instrument’s engineers build and market the first commercial device. In 1955 Jules Andrus and Walter Bond (Andrus & Bond, 1958) [18], adapted photoengraving techniques from printing technology to enable precise etching of diffusion windows in Si wafers. In September 1955 William Shockley (Shockley, 1955) [19] founded Shockley Semiconductor Laboratory and develops Northern California’s First prototype silicon devices while training young engineers and scientists for the future Silicon Valley. In 1958, Fairchild Semiconductor produced double-diffused silicon mesa transistors to meet demanding aerospace applications (Moore, 1998) [20]. In the year 1959 Jean Hoerni (Hoerni, 1962) [21] develops the planar process to solve reliability problems of mesa transistor, thereby revolutionizing semiconductor manufacturing. In the same yearRobert Noyce (Noyce, 1961) [22] builds on Jean Hoerni's planar process (Hoerni, 1962) [21] to patent a monolithic integrated circuit structure that can be manufactured in high volume. Then Dawon Kahng fabricate working transistors and demonstrate the first successful MOS field-effect amplifier (Kahng, 1963) [23]. Jay Last (Norman, Last & Haas, 1960) [24] leads development of first commercial IC based on Hoerni’s planar process (Hoerni, 1962) [21] and Noyce’s monolithic approach (Noyce, 1961) [22]. In 1961 computer architect Seymour Cray funds development of first silicon device to meet the performance demands of world’s fastest machine. The 2N709 (FT-1310) n-p-n device was introduced in July 1961 as first silicon transistor to exceed germanium speed [25]. The size, weight, and reduced power consumption of integrated circuits compared to discrete transistor designs justify their high cost in military and aerospace systems. Diode Transistor Logic (DTL) families create high-volume market for digital ICs but speed, cost, and density advantages establish Transistor Transistor logic (TTL) as the most popular standard logic configuration by the late 1960’s (Ruegg & Beeson, 1961) [26]. General Microelectronics introduces first commercial Metal-Oxide-Semiconductor (MOS) integrated circuit when a 2-phase cock scheme (Norman & Stephenson, 1969) was used to to design a 20-bit shift register using 120 p-channel transistor. Gordon Moore, Fairchild Semiconductor’s Director of R&D, prediction of the rate of increase of transistor density on an integrated circuit and establishment of a yardstick for technology progress (Moore, 1964) [28]. Improvement on the reliability, packing density, and speed of MOS ICs with a silicon-gate structure and designof the first commercial silicon-gate IC, the Fairchild 3708 (Faggin & Klein, 1970) [29]. The Microma liquid crystal display (LCD) digital watch (Forrer, 1972) [30] is the first product to integrate a complete electronic system onto a single silicon chip, called as System-On-Chip or SOC.

This review is done to provide the importance of silicon as a semiconductor, which has a wide use in electronics, Telecommunication, and in other fields. This paper includes the work done on silicon by prominent scientist and a broad review of properties, growth techniques for silicon crystal , applications and latest research done till date. Comparison of Czochralski growth method and Floating-zone method is also presented.

2. Preparation

2.1. Preparation process of Si for devices

Semiconductor devices and circuits are fabricated using wide variety of mechanical, chemical, physical & thermal process. The flow diagram for typical Si preparation process is shown in figure 1 below. Preparation of Si single crystal substrate with mechanically & chemically polished surface is the First step in lengthy process of device fabrication. The main requirement is that Si which is used it must be extremely pure and secondly, it must have large diameter crystals. Also, the cost of production, specifications of material, are important in today’s aspect.

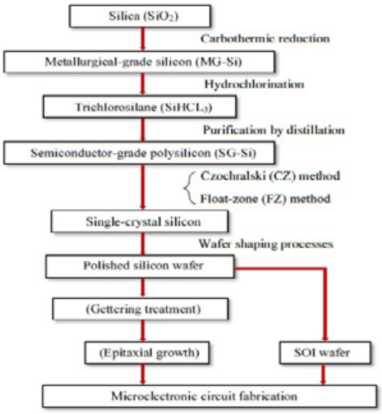

Figure 1. Flow diagram for typical Si preparation process

2.2. Single Crystal growth

There are two main methods of single crystal growth, one is Float-zone method and the other is Czochralski method (Pulling method). The first one, Float-zone (F-Z method) was invented by Theurer. It is the reactivity of liquid Si with material used for crucible. It crystallizes Si without any contact with the crucible material so that a crystal of any semiconductor purity can be grown. Some properties of F-Z are,

- It has higher purity compared to C-Z crystal.
- F-Z silicon contains less than 10^{16}atoms/cm^{3}oxygen impurities.
- F-Z silicon has resistivity of between 10-200 Ωcm.
- F-Z silicon is used to fabricate semiconductor power devices for relative voltage range of 750-1000V.
- F-Z Si is mechanically weaker and vulnerable to thermal stress, to overcome this F-Z Si crystal was grown with doping impurities like O_2 and N.
- When doped with Nitrogen and Oxygen at concentration of 1.5×10^{15} atoms/cm^3 or 1-1.5×10^{17} atoms/cm^3 respectively resulted in increase of mechanical strength.

Czochralski Method was invented by J.Czochralski and modified by Teal & Little. This modified version is widely applied to single-crystal growth. They were the first to grow single-crystal of Ge 8 inch in length and 0.75 inches in diameter. There are 3 main steps in C-Z crystal growth a) melting polysilicon, b) Seeding. c) Growing. Some important steps are,

- Polysilicon chunks are placed in quartz crucible and melted at 1420^{o}C in an inert ambient.
- A seed crystal with any crystal orientation is dipped into melt until it melts itself, then seed is taken outside of melt to form a neck. Here inert gas flow downwards through pulling chamber in order to wipe out products SiO and CO.
- As diameter is increased conical part and shoulder are grown.
- Lastly, by pulling rate control, a cylinder part of body with constant diameter is grown. Pulling rate is reduced to tail end of crystal due to increasing heat radiation from crucible wall.

2.3 Other crystal Growth method

2.3.1 Czochralski growth with Applied Magnetic Field (MCZ)

This method was first applied to crystal growth of indium antimonide via horizontal boat technique and horizontal zone melting technique. Through this we came to know that a magnetic field of sufficient strength can suppress the temperature fluctuation that accompany melt convection and can dramatically reduce growth striations.

2.3.2. Continuous Czochralski method (CCZ)

For replenishing a quartz crucible with melt economically, is to continuously add feed as crystal is grown and to maintain the melt at constant volume. In addition to saving crucible cost the Continuous Charging Czochralski (CCZ) method provides an ideal environment for Silicon crystal growth. This method solves most problems related to inhomogeneity in crystal grown by conventional CZ method.

Combination of MCZ and CCZ is expected to provide ultimate crystal growth method, giving ideal Si crystal for a wide variety of micro-electronic application. It is also used to grow high-quality Silicon crystals used in micro-electronics devices.

2.3.3. Neckingless Growth Method

It is a critical step during CZ crystal growth, growing 3-5 mm in diameter, because it eliminates grow-in dislocation. This method is used since 50 years in the industry. A thin neck (3-5mm) can't support large crystal diameter (>300 mm, weight >200 kg) needs larger diameter necks. It is estimated that large diameter necks 12mm in diameter can be C-Z support crystal as heavy as 2000kg

3. Properties of Pure Silicon

CATEGORY	PROPERTIES	VALUES	REFERENCE
In Periodic table:	1.Atomic number 2.Atomic weight 3.Group 4.Period 5.Block 6.Electronic configuration	14 28 14 3 p-block [Ne] $3s^2\ 3p^2$	
Crystal form:	1.Lattice spacing(300K) 2.Density at 300K 3.Critical pressure 4.Critical Temperature	0.431 nm $2.329 g/cm^3$ 1450 atm $4920\ ^oC$	
Band structure	1.Dielectric constant(300K) 2.Effective density of states (conduction, Nc T=300K) 3.Electron affinity 4.Energy Gap E_g at 300 K (Minimum Indirect Energy Gap at 300 K) 5.Energy gap E_g at ca. 0 K (Minimum Indirect Energy gap at 0 K) 6.Minimum Direct Energy Gap at 300 K 7.Intrinsic Debye length 8.Intrinsic carrier concentration	11.9 $2.8\times10^{19} cm^{-3}$ 133.6 kJ/mol 1.12 eV 1.17 eV 3.4 eV 24 µm $1\times10^{10}\ cm^{-3}$	www.el-cat.com/silicon-properties.htm [31]
Thermal:	1.Melting point 2.Boiling point 3.Specific Heat 4.Conductivity(300K) 5.Heat of Fusion 6.Heat of vaporization	$1414\ ^oC$ 3538 K $0.7 J/gx^0C$ 14 W/mK 39.6 kJ/mol 383.3	

	7.Heat of atomization	kJ/mol 452 kJ/mol	
Electrical:	1.Mobility e^- 2.Mobility holes 3.Electronegativity 4.Breakdown Field 5.Diffusion coefficient of e^- 6.Diffusion coefficient of holes 7.Electron thermal velocity 8. Hole thermal velocity	1400 cm^2/Vs 450 cm^2/Vs 1.8 Pauling 3×10^5 V/cm 36 cm^2/s 12 cm^2/s 2.3×10^5 m/s 1.65×10^5 m/s	
Mechanical:	Bulk modulus Density Hardness Young's modulus (100) Shear modulus Poissons ratio	$9.8\times10^{11}dyn/cm^2$ 2.329 g/cm^2 7 mohs scale 129.5 GPa 64.1 GPa 0.22-0.28	
Optical	1.Dielectric constant (static) 300 K 2.Infrared refractive index n(λ) 300K 3.Radiative recombination coefficient 300 K 4.Optical photon energy 300 K 5. Absorption coefficient 300 K , $\lambda \geq 5\mu m$,	11.7 n = 3.42 $n = 3.38(1 + 3.9\cdot10^{-5}\cdot T)$ 77K < T < 400 K $1.1 \times 10^{-14}\ cm^3\ s^{-1}$ 63 meV $\alpha_n = 10^{-18}\cdot n_o\cdot\lambda^2$	(Schroeder et al ,1978) [32]

4. Properties of Doped Silicon

Boron doped	1.Ionization energy 0.045 eV 2.Resistivity 13.51 ohmcm 3.Mobility 462 cm^2/Vs (concentration 1.000e15 a/cm^3)	www.el-cat.com/silicon-properties.htm [33]
Arsenic doped	1.Ionization energy 0.054 eV 2.Resistivity 4.594 ohmcm 3.Mobility 1359 cm^2/Vs	

	(concentration 1.000e15 a/cm^3)	
Phosphorus doped	1.Ionization energy 0.045 eV 2.Resistivity 4.582 ohmcm 3.Mobility 1362 cm^2/Vs (concentration 1.000e15 a/cm^3)	
Antimony doped	1.Ionization energy 0.039 eV 2.Resistivity 4.861 ohmcm 3.Mobility 1284 cm^2/Vs (concentration 1.000e15 a/cm^3)	

The measurement of the temperature dependence of resistivity and Hall coefficient in gold-doped silicon (Collins, Carlson & Gallagher, 1957) [34], shows an acceptor level at 0.54 eV from the conduction band and a donor level at 0.35 eV from valence band. The distribution coefficient for gold in silicon is 2.5×10^{-5}.

The properties of iron and copper doped silicon (Collins & Carlson, 1957) [35], measurements showed that Iron introduces a donor level into silicon at 0.04 eV from valence band and converts to a level of 0.55 eV from conduction band at room temperature and the conversion is reversible in range 70^{o}-200^{o}C. The electrically active solubility was 1.5×10^{16} cm^{-3} at 1200^{o}C and distribution coefficient was 8×10^{-6}. Copper introduces donor level at 0.24 eV and acceptor level at 0.49 eV from the valence band. Electrical activity in sample was 5×10^{14} cm^{-3} out of 10^{18} cm^{-3} at 1200^{o}C.

Properties of silicon doped with nickel was measured (Tokumaru, 1963) [36]. The measurements of temperature dependence of resistivity and Hall coefficient of nickel-doped silicon indicated that nickel act as a acceptor impurity in silicon, introducing two acceptor levels, namely, 0.35±0.03 eV from conduction band and 0.23±0.03 eV from the valence band.

The detailed galvanomagnetic measurements on high purity, high resistivity nickel doped silicon (Chau, 1970) [37],which confirm the existence of two acceptor levels lying 0.24±0.01 and 0.37±0.01 eV from the valence and conduction bands, respectively.

Investigation on oxidation characteristics of heavily doped silicon in dry and wet (95^{o}C HO) oxygen ambient over temperature range 920^{o}-1200^{o}C for oxide thickness of 0.10-1.0µ was shown (Deal & Sklar, 1965) [38]. Silicon was uniformly doped with boron (1×10^{16} to 2.5×10^{20} cm^{-3}) and phosphorus (4×10^{15} to 1.5×10^{20} cm^{-3}). It was observed that Boron concentrations greater than 1×10^{20}cm^{-3} cause an increase in oxidation rates at all temperature, greatest effect occurring in dry oxygen Boron. At 920^{o}C, phosphorus concentrations of 1×10^{19} cm^{-3} or more resulted in significant increase of oxidation rates. The latter effect was most pronounced in wet oxygen.

5. Applications

Roughly ten million metric tonnes of ferrosilicon and silicon metal are refined each year, the majority of silicon used commercially is actually in the form of silicon minerals, which are used in the manufacture of everything from cement, mortars, and ceramics, to glass and polymers.

Ferrosilicon, is the most commonly used form of metallic silicon. Since its first use around 150 years ago, ferrosilicon has remained an important deoxidizing agent in the production of carbon and stainless steel. Today, steel smelting remains the largest consumer of ferrosilicon

Ferrosilicon has a number of uses beyond steelmaking, though. It is a pre-alloy in the production of magnesium ferrosilicon, a nodulizer used to produce ductile iron, as well as during the Pidgeon process for refining high purity magnesium. Ferrosilicon can also be used to make heat and corrosion resistant ferrous silicon alloys as well as silicon steel, which is used in the manufacture of electro-motors and transformer cores.

Metallurgical silicon can be used in steelmaking as well as an alloying agent in aluminum casting. Aluminum-silicon (Al-Si) car parts are lightweight and stronger than components cast from pure aluminum. Automotive parts such as engine blocks and tire rims are some of the most commonly cast aluminum silicon parts.

Nearly half of all metallurgical silicon is used by the chemical industry to make fumed silica (a thickening agent and desiccant), silanes (a coupling agent) and silicone (sealants, adhesives, and lubricants). Photovoltaic grade polysilicon is primarily used in the making of polysilicon solar cells. About five tons of polysilicon is needed to make one megawatt of solar modules.

Currently, polysilicon solar technology accounts for more than half of the solar energy produced globally, while monosilicon technology contributes approximately 35 percent. In total, 90 percent of the solar energy used by humans is collected by silicon-based technology.

Monocrystal silicon is also a critical semiconductor material found in modern electronics. As a substrate material used in the production of field effect transistors (FETs), LEDs and integrated circuits, silicon can be found in virtually all computers, mobile phones, tablets, televisions, radios and other modern communication devices. It is estimated that more than one-third of all electronic devices contain silicon-based semiconductor technology.

Finally, the hard alloy silicon carbide is used in a variety of electronic and non-electronic applications, including synthetic jewelry, high-temperature semiconductors, hard ceramics, cutting tools, brake discs, abrasives, bulletproof vests and heating elements.

Silicon has a wide range of application especially in growing electronics industry. For example, Silicon is frequently paired with aluminium to produce a silicon-aluminum alloy, which can be used in casting and manufacturing large metallic parts. Overall silicon-aluminum alloys are distinguished by their high tensile strength. Silicon semiconductor is used in devices like transistors, printed circuit boards and integrated circuits. For transistors, the material silicon is doped by adding a small impurity which enables the electrons to move around, conduct electricity and generate reliable semiconductors for voltage. When Silicon is heated into a molten state, Si can be formed into semiconductive wafers to serve as the base for integrated circuits or microchips. Silicon used in semiconductor device manufacturing is currently fabricated into boules that are large enough in diameter to allow the production of 300 mm (12 in) wafers. In effects first observed in the 1870s, some semiconductors respond to light by producing an electric current (the photovoltaic effect) or becoming able to conduct current (the photoelectric effect). Photovoltaic (solar) cells are used to provide electrical power to remote locations, on satellites, and, in combination with storage batteries, for some outdoor lighting. Still other semiconductors give off light when they gain electrons. Semiconductor lasers are often paired with photoelectric cells in automatic doors, burglar alarms, bar-code readers, and fiber-optic communications devices. In the latest study, electrical engineers at Stanford have identified the new ultrathin semiconductor, hafnium diselenide and zirconium diselenide, materials that exceeded some of silicon powers. Both the ultrathin semiconductor rust, which is more desirable than silicon. They form technologically desirable high-K native dielectrics HfO_2& $ZrSe_2$ which enable lower power operation than is possible with silicon and its silicon oxide insulators. When diselenides were shrink to atomic thinness showed the band-gap 0.9 to 1.2 eV (bulk to monolayer) just in right range as of silicon. Electronic measurement revealed promising performance (on/off ratio > 10^{-6}, on current ~ 30 µA/µm). Diselenides can also be fashioned into circuits, just three atoms thick or about two-thirds of a nanometers which silicon cannot do (Mleczko et al, 2017) [39]. Researchers at Princeton University has created a piece of silicon-based hardware that can control quantum behavior between several electrons and with relatively high precision. An efficient resonantly driven CNOT gate for electron spins in silicon (Zajac et al, 2018) [40]. Single-qubit rotations having fidelity > 99%, its quantum dot device architecture enabled multi-qubit algorithm in silicon.

6. Conclusions

- Review of development of silicon as a semiconductor device, growth techniques used for silicon crystal, its properties and applications is reported in the paper.

- Float-zone method and Czochralski method for growth of silicon crystal are compared along with CCZ and MCZ.
- Significant alteration is observed in properties of pure silicon due to addition of impurities.
- Review envisaged that silicon is extensively used in semiconducting technology and in growing electronic industry and could not be replaced by other semiconducting material other than germanium till date.
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